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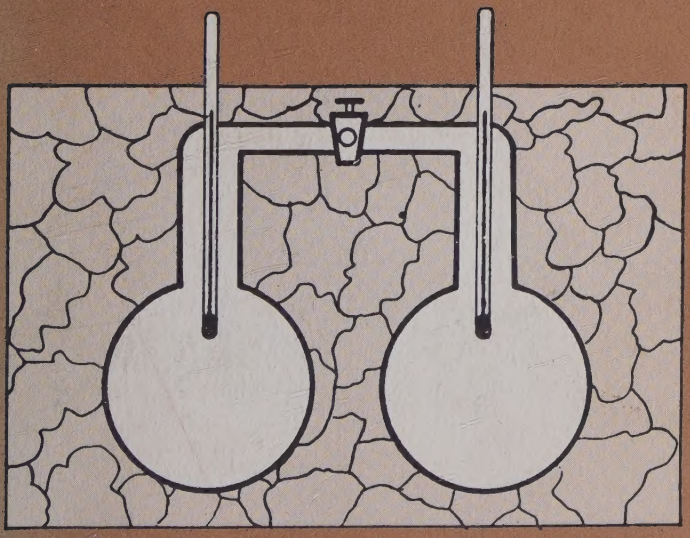
Leonard B. Loeb

the kinetic theory of gases



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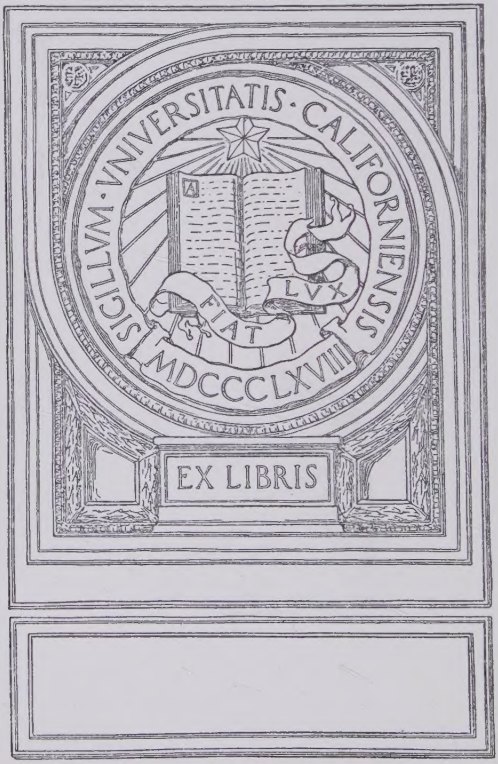

THE KINETIC THEORY OF GASES

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THE KINETIC THEORY OF GASES

Being a Text and Reference Book Whose Purpose Is to Combine the Classical Deductions with Recent Experimental Advances in a Convenient Form for Student and Investigator

BY

LEONARD B. LOEB

Professor of Physics in the University of California

THIRD EDITION

DOVER PUBLICATIONS, INC.

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This new Dover edition, first published in 1961, is an unabridged republication of the second edition (1934) of the work first published by the McGraw-Hill Book Company, Inc. in 1927. The present edition also contains a new Preface and Summary of Recent Progress by the author.

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TO MY TEACHERS:

ROBERT ANDREWS MILLIKAN

AND

EXUM PERCIVAL LEWIS

TO WHOM THE INSPIRATION FOR THIS BOOK IS LARGELY DUE

140788

PREFACE TO THE DOVER EDITION AND SUMMARY OF RECENT PROGRESS

I. Preface

Nearly thirty-five years have passed since the first preface to *The Kinetic Theory of Gases* was written and twenty-seven since the preface to the second edition. During those years, science in general, and especially physics has undergone an almost incredible expansion, with many changes—most for the best, yet some of doubtful value.

During World War I, American industry discovered chemistry as an indispensable tool. World War II and its continuation in the form of the cold war focused the attention of industry and, what is perhaps less desirable, of the general lay public on physics. The fantastic success of organized mass research and engineering efforts in capitalizing on basic discoveries prior to 1940 to produce such marvels as television, radar, proximity fuses, jet propulsion, electronic computers, cyclotrons, bevatrons, and also the applications of nuclear fission and fusion manifested in the atom and hydrogen bombs and in the benefits and hazards of thermonuclear power, have led to a dangerous misconception in the minds of industry and the public. This is the belief that all that is needed in order to achieve almost any desired technical objective is a sufficiently extensive crash program with adequate technical personnel and a superfluity of funds. To anyone who has lived through the recent three generations of scientific advance and followed the utterly unpredictable, erratic, and often painfully slow advance in antecedent discovery and knowledge, the fallacies of this viewpoint are strikingly clear. Even with the genius of a Rutherford, the Curies, Chadwicks, and their many forgotten but outstanding colleagues, it took forty years of painstaking basic study before nuclear power could be harnessed for mankind, though the possibility was evident to

all shortly after 1896. Unfortunately, Rutherford himself did not live to see his dream realized.

A careful study of any of the marvels of scientific achievement we have would reveal the slow and often fortuitous discoveries of countless workers, many now forgotten, whose discoveries laid the foundations of our era. The underlying reason for the fallacy that massive expenditure will necessarily lead to a scientific objective lies in not recognizing that no one genius nor even any collection of geniuses and able workers is omniscient. It is impossible to plan any program which could guarantee that the basic facts or knowledge vital to a project can be found at once. All too often it is the independent worker carrying on a study in a seemingly off-track area who succeeds in uncovering the missing information. What group effort and expenditure of vast sums can do—often under such an urgent stress as produced by war—is to marshal the combined resources by rapidly exploiting existing basic knowledge for a difficult technological feat.

Thus, for example, it was obvious to physicists throughout the world acquainted with nuclear physics that an atom bomb was possible once fission had been discovered. As a case in point, the author, teaching a course in undergraduate nuclear physics, within four months of the announcement of fission had his class calculate the approximate mass of the U^{235} needed for a bomb. The value calculated was within a factor of 2 or 3 that of the bomb dropped on Hiroshima. He then had them calculate how long it would take with existing techniques to amass that quantity of U^{235}. The atom bomb project by mass effort and the expenditure of a billion dollars accomplished the engineering feat using basic discoveries and techniques already known. The plutonium bomb was derived from the chance basic investigations of McMillan and Seaborg into making transuranic elements; prior to the Manhattan project, there was no idea of exploiting this research for a bomb. Likewise, the elements indispensable to radar were known almost eight years or more before it was developed into a practical device. Only because of the urgencies of a war for national survival were practical applications quickly developed by such programs; other-

wise, they would have developed more gradually as uses or needs furnished a sufficiently strong incentive.

The net result of the tremendous scientific and technological effort expended during the post-World-War-II period in a considerable range of fields of study was that we were left with an unbelievable wealth of new instruments available to scientific and technological advance. The consequences of this technological revolution and the continued expenditure of vast sums on research and development for defense and industrial purposes must be considered: first, the "mass production" of scientific workers leaves some with a training less than what could be desired. Second, an enormous volume of scientific and technical publication has been created, some good but also largely buried in reports of limited circulation. Third, the variety of problems to be overcome has created a proliferation of fields of scientific interest, each one becoming more and more highly specialized. Thus, while the author in 1938 was able to keep abreast of the major advances in such diverse fields as nuclear physics, gaseous electronics, kinetic theory, atomic physics, and solid state physics, all he can do today is to keep up with the significant advances in gaseous electronics and atomic physics.

These three factors, together with the greatly increased costs of publication, in turn exert changes in the textbooks and scientific monographs basic to instruction and research. The problem of textbooks, vital to the instruction of future physicists, is still further complicated by another factor—the remarkable success of modern theoretical physics in unifying, systematizing, and portraying physics. There is in such formulations and in their use in solving problems for which they were devised an aesthetically satisfying compactness and seeming simplicity. These formulations are basically only symbolical representations couched in the language of mathematics and express the results of and deduction from experimental work. They are valid only to the extent to which they are experimentally verifiable. Thus, taken as a whole, they represent only a partial picture of physics. Unless the user knows how they were derived from experiment and to what extent they are capable of extra-

polation beyond experiment, he is on dangerous ground. Furthermore, unless by analogy or experience the research man has learned to derive laws from experiment, how will he, groping into the unknown, in turn be able to extend existing theory? Those questions are quite pertinent to the situation facing the future student.

Because of the vast mass of material, the many fields to which a student of today must be introduced, and the pressure of rapid mass production of scientists, textbooks should have large scope, careful selection of material, and an exceptionally efficient organization. Unfortunately, the cost of production of books today limits size essential to adequate coverage since, in general, books in excess of 500 pages are prohibitively expensive. Efficient organization can most easily be achieved by emphasis on the theoretical, systematic, and inductive formulation devoid of the experimental details. Thus, the trend in books today is away from extended and useful content and more and more towards the purely formalistic approach of theoretical physics. This is especially so in the area of upper division and graduate collegiate texts. In the lower division the same trend leads to the danger of a much more superficial treatment than was true in the past.

There is no time in much of today's instruction for giving the experimental background upon which theory is based. In consequence, the recently trained young physicist is losing his basic physical intuition. It is only a rare teacher today who has time to tell his students how the great discoveries of the past and their symbolic interpretations came to be made. No student of physics today knows even the rudiments of the developmental history of the field which he is learning and in which, ultimately, he will be experimenting. He assumes that the beautiful theory of today sprang full blown from the head of an Einstein or a Bohr. This prompts one to wonder whether, despite the great technical advances and the proliferation of knowledge, the physicists will not soon lose the art of discovery or at least will become less proficient in this field of endeavor.

It is against this background that those of us who have been active as experimental research pioneers as well as

teachers welcome the paperbacks and especially publishing houses like Dover Publications which make available to today's student the pioneering works and textbooks of the past and show how our modern science developed. In this way they aid those more thoughtful and thorough students to broaden their understanding and create for them a living experimental science instead of mere formalism.

When the first edition of the *Kinetic Theory* was published, relatively few physicists were acquainted with the kinetic theory. There were few physics courses dealing with the subject, and these were mostly on the graduate level. Chemists were still largely espousing the cause of energetics and the thermodynamical approach as opposed to that of the mechanistic molecular theory. Concern about this situation was clearly reflected in the preface to the first edition. As the second edition was written, the greater proportion of physicists were being trained in kinetic theory, since they were dealing with the extra-nuclear atom, quantum theory, molecular physics, and were branching out into solid state and surface physics. At this time we were nearing the end of the rapid advance of atomic theory, before the transition to an era dominated by the nuclear studies. In this era, this book had been instrumental in introducing many young physicists to the kinetic theory concepts with which they were to help reformulate the analysis of atomic and nuclear structure.

Until 1932, nuclear research could only be carried out in laboratories having access to powerful sources of radium. By 1932, Lawrence had developed the cyclotron which within two or three years was to yield directed, charged particle fluxes exceeding those from radium at eight million volts and over. Chadwick's discovery of the neutron together with Anderson's discovery of the positive electron in that year, and the Curie-Joliot creation of artificial radioactivity in 1934, followed within five years by Hahn's discovery of nuclear fission, completed the transition.

The nuclear age was well on its way, and with it came a complete change in emphasis of the directions of physical research. With the entrance of more kinetic theory into the instruction of the creators of the nuclear age, it is not sur-

prising that many of the conceptual developments guiding advance in nuclear physics came from atomic physics, into which had gradually been incorporated the basic principles of the kinetic theory of gases and the rapidly developing quantum mechanics. In fact, the concept of interaction cross sections of electrons, X and γ rays and protons, α particles and neutrons came directly from the kinetic theory as did many of the other analytical approaches in this field involving energy distributions, diffusion, force fields, and statistical mechanics.

The author would hope that in a small measure this book with its two previous editions, many printings and its extended use both in this country and England added its small share in preparing the way and stimulating this advance. In any event, the book had served a very useful function for some twenty-seven years before it was retired from publication though still enjoying a continued and moderate sale. As a book that is closely related to the developmental and experimental aspects of the field, it has not been superseded to date. Two outstanding books of the same title but of a more theoretical character, one by E. H. Kennard and the other by R. D. Present, have appeared. Kennard's book has proven of great use, especially since it introduces the student in a readily comprehensible fashion to the very powerful Boltzmann methods of analysis of transport phenomena of which daily use is made in the present era. The other book, by Present, is a very beautiful inductive and somewhat more advanced treatise written in a particularly clear, readable, and very compact form.

Other than these two books, the shifting emphasis in textbooks and courses of instruction has largely shirked the presentation of kinetic theory as such in upper division and graduate collegiate courses of instruction. What courses are given are largely those in graduate school in combination with some thermodynamics and much more statistical mechanics. In keeping with the spirit of the modern trend, lower division texts on general physics of a comprehensive but increasingly formal and perhaps superficial character include as part of a general treatment a few of the important elementary concepts, such as those of mean free paths

and energy distribution. These treatments yield just enough information to enable the student to understand the significance of cross sections, but yield no insight into force fields and their significance.

In consequence, the reprinting of this book with its great emphasis on sequential development of the subject, its strong dependence on experiment throughout, and, above all, with certain of its chapters dealing with the extension or even limitations placed on classical Newtonian kinetic theory by force fields and quantum mechanics continues to render an almost irreplaceable service. The chapter on low pressure phenomena and surface effects is still of immense use, particularly since many of the questions raised and discussed there are now amenable to study under the modern vacuum techniques. The book's value lies further in the fact that up to the date of its issue, it contained under one cover the chief literature and major advances in a plethora of new fields which today in themselves would require separate treatises.

II. Recent Advances

Since this aspect presents one of the major assets of the book, it is proper in reprinting to initiate this undertaking by including a brief résumé of some of the striking new advances with appropriate references.

The résumé may well start by presenting one of the most beautiful illustrations of the adventitious nature of industrially *useful* scientific discovery on record. The discovery comes from one of the most abstruse generalized analyses of transport phenomena done by Chapman and Enskog independently and nearly contemporaneously. This matter is just mentioned in a superficial fashion in a paragraph on page 275 of this book and previously was generally ignored in most textbooks. It consists of the prediction of a phenomenon known as *thermal diffusion*. This occurs as a consequence of repulsive forces between molecules of the form Gr^{-n} with n greater than 5, and leads to terms in the expression for diffusion depending not only on variation of number density with distance but also with variations of temperature and pressure along the same axis. Thus a tem-

perature gradient in a long tube will cause a diffusion of molecules or atoms, in a mixture of two species with different masses, to the two ends of the tube, producing changes in number densities at the two ends. The separation had been experimentally tested by Dootson and later by Ibbs and had been found to occur, though the effects were small. No one would have dreamed of the practical exploitation of the phenomena. Yet, when physicists were faced with the formidable task of the separation of the two uranium isotopes of masses 235 and 238, the initial enrichment of U^{235} was accomplished, using the volatile uranium hexafluoride, by thermal diffusion preceding the magnetic separation in the Calutron at Oak Ridge. The physics of the process up to pilot plant design was the work of Abelson and Ross Gunn of the Naval Research Laboratory.

One of the areas in which the greatest scientific advances have been made is in the field of molecular beams. Stern and Estermann improved the earlier techniques using hot-wire Pirani detector gauges and surface ionization measurements with Na atoms. They were even able to measure the deflection of atoms in a molecular beam by the earth's gravitational field using a method of compensating fields. These measurements and the techniques are reported by O. Stern, *Phys. Rev.* Vol. 51, 852 (1937) and I. Estermann, O. C. Simpson, and O. Stern, *Phys. Rev.* Vol. 53, 947 (1938) and 65, 346 (1944). The general techniques are summarized by I. Estermann, *Rev. Mod. Phys.* Vol. 18, 300 (1946) and also in *Recent Research in Molecular Beams* by various authors (Academic Press, New York, 1959). Molecular beams were used in the measurements of dipole moments of HCl by Estermann and Fraser, *J. Chem. Phys.* Vol. 1, 390 (1933). I. I. Rabi, working in Stern's laboratory, developed new and more accurate magnetic fields for deflection of the beams [*Z. Physik,* Vol. 54, 190 (1929)].

In 1932, with improved techniques, Estermann and Stern developed methods for determining the magnetic moment of the proton, which is about 10^{-3} of that for the electrons [see *Z. Physik,* Vol. 85, 17 (1933) and Vol. 86, 132 (1933)]. The method was adapted by Rabi for the measurement of proton spin and nuclear magnetic moments by deflecting H

atoms in inhomogeneous magnetic fields created by parallel wires, with wires parallel to the beam, and detecting the beam by reduction of WO_2 on a plate. This was reported in the *Phys. Rev.* Vol. 46, 157 (1934). Two opposing magnetic fields of different lengths were later used in conjunction with a Pirani gauge detector and reported in the *Phys. Rev.* Vol. 50, 472 (1936). For this work and his later developments Rabi was awarded the Nobel Prize.

Work continued in Rabi's laboratory, and P. Kusch added the element of using a magnetic field perpendicular to the opposing fields parallel to the beam to decouple the nuclear and electron spins and then using a high frequency alternating electrical field to alter the spins. By changing the frequency to synchronize the transitions so as to cause transmission of the beam, the molecular beam resonance method was developed and reported in the *Phys. Rev.* Vol. 53, 384 (1938). This is sometimes called the flip-flop or flopping method. As time went on and with the great advances in detecting and amplifying techniques, the method has become a most powerful tool for all sorts of basic atomic and nuclear studies. In 1952, it was used by Rabi [*Phys. Rev.* Vol. 87, 379 (1952)] and Senitzky, Rabi, and Perl [*Phys. Rev.* Vol. 98, 611 (1955)] to study the hyperfine structure of the 3 P state of Na^{23} and was later extended to Rb^{85} and Rb^{87}. The atoms were optically excited in the depolarizing and oscillating field region. The surface ionization beam detector was used in conjunction with a mass spectrometer. These techniques have led to clocks, now available commercially, using the atomic resonance properties accurate to one part in 10^{10}. For his part in the development of the radio-frequency resonance technique, Kusch was also awarded the Nobel Prize. The most specialized techniques in this area have been developed by W. A. Nierenberg at Berkeley for the measurement of the nuclear moments of the small quantities of many new short-lived radioactive isotopes created in the cyclotron. Study of these are of immense value in interpreting nuclear structure and behavior. The work started with a zero moment device but was converted to a Zacharias-Rabi flop-in apparatus in 1955. Publications are by Bemski, Nierenberg, and Silsbee,

Phys. Rev. Vol. 98, 470 (1955); Hobson, Hubbs, Nierenberg, and Silsbee, *Phys. Rev.* Vol. 96, 1450 (1954); Hobson, Hubbs, Nierenberg, Silsbee, and Sunderland, *Phys. Rev.* Vol. 104, 101 (1956); Nierenberg, Shugart, Silsbeee, and Sunderland, *Phys. Rev.* Vol. 104, 1380 (1956); and Hubbs, Nierenberg, Shugart and Worcester, *Phys. Rev.* Vol. 105, 1928 (1957). See also *Recent Research in Molecular Beams* Chap. 1, p. 9 (Academic Press, New York, 1959).

Probably one of the greatest advances in the applications of kinetic theory came as a result of the microwave breakdown studies of gases initiated at the Massachusetts Institute of Technology by W. P. Allis and S. C. Brown and their students. As a result of the intensive development of radar at that school during World War II, it was natural that the electrical breakdown of gases under the influence of microwave became of interest. Here the kinetic theory involves the motion and gain and loss of energy of electrons in a gas where frequencies of oscillation of the electrons as well as their amplitudes of motion are respectively commensurate with the times and distances between collisions in the gas. The initial analysis of the process by H. Margenau [*Phys. Rev.* Vol. 69, 508 (1946) and Vol. 73, 297 (1948)] started a train of researches using the very intense and uniform types of ionization produced by ultra-high-frequency- ($\sim 3 \times 10^9$ cycles/sec) created electromagnetic fields in a quartz cell and the analysis of the resonance by means of the intensity of transmission of a weak probing signal or a similar device. This technique opened up a wide range of basic physical investigation of atomic and ionic properties. The beautiful kinetic theory solutions possible by use of the Boltzmann transport equation and more esoteric analyses by Allis and also by T. Holstein and his associates at Westinghouse added much new information and made possible much more to come. The value of this method is that it gives more nearly uniform masses of ionized gas with high and isotropic electron density, a situation previously not attainable. This enabled studies of diffusion and recombination previously not achievable to be carried out. The description of this method can be found in Loeb, *Basic Processes of Gaseous Electronics,* p. 502 ff., (University of

California Press, Berkeley, 1955). The theory is given by T. Holstein in *Phys. Rev.* Vol. 70, 367 (1946); S. C. Brown, *Encyclopedia of Physics,* edited by S. Flugge, Vol. XXII, p. 531, (Springer-Verlag, Berlin, 1950).

Actually, the whole field of gaseous electronics and its associated atomic structure have necessitated the constant application of the kinetic theory of gases, beginning with the early studies of Langevin on electron and ion collision processes in fields of gases reported in this book, but carried much further by M. J. Druyvesteyn, just prior to World War II, and by many others. Some of this work on the experimental and theoretical side can be found in the author's *Basic Processes of Gaseous Electronics,* Chapter I (especially p. 142 ff.); Chap. II (pp. 235-242); Chap. III (pp. 272-328); Chap. VIII (p. 712 ff.); and in Allis' article in the *Encyclopedia of Physics,* Vol. XXI, p. 383, (Springer-Verlag, Berlin, 1956). Further applications of the theory are coming into use by the physicists and chemists in the kinetic studies of the complicated structure of the ions in gases just beginning to be investigated (see *Basic Processes in Gaseous Electronics,* Chap. I, pp. 105-109 and pp. 118-141).

Simultaneously, the field of quantum mechanics and its application was developing further during the years preceding World War II and becoming more complete and strongly entrenched in the following years. This has led to a considerable physics of collision processes in gases, which are well portrayed in Mott and Massey, *Theory of Atomic Collisions,* 2nd ed. (Oxford Press, 1949); Mott and Sneddon, *Wave Mechanics and its Applications* (Clarendon Press, 1948); and Massey and Burhop, *Electronic and Ionic Impact Phenomena* (Oxford Press, 1952).

In Chapter VII, the study of rarefied gases and surface phenomena was reported as it had developed up to 1934. Hurlbut (see *J. App. Phys.* Vol. 28, 844, 1957), under Kunkel and the author, carried on studies of the accommodation coefficient of specular reflection of common molecules from metal surfaces using molecular beam techniques at various angles. The work was supervised by Estermann, and integration over all angles leads to correlation with Maxwell's

coefficient of slip. This study, under the auspices of the Richmond Engineering Field Station low pressure wind tunnel project at the University of California, is still being carried on.

Little advance in this field was possible for some time since surfaces could never be properly freed from gases, and pressures rarely could be reduced below 10^{-8} mm. of Hg. In 1949, D. Alpert and his co-workers at Westinghouse discovered means of overcoming the two worst difficulties. The first consisted in the perfecting of a bakeable metal diaphragm valve made of Cu and Kovar that replaced the greasy stopcocks with all their contaminating influence. While most massive metals which are used in the valves have much absorbed gas, they can be heated to some 400°C in a good vacuum and lose enough gas from their surface layers so that when cooled to room temperature little further gas is evolved. The valve consists of a bakeable cup-shaped base of stainless steel or monel metal with a pure copper block inserted at its bottom which serves as the valve seat. An exhaust tube of Cu of about 3 mm. diameter goes through the cup base off axis while a second tube going to the system is placed axially. About 1 cm. above the Cu seat block and orifice, a Kovar diaphragm carrying the cylindrical Kovar valve stem of appropriate diameter at its center is brazed to a seat on the cup with an Ag-Cu solder using no flux in an H_2 atmosphere. The Kovar valve stem has a carefully polished conical tip that is sealed in the orifice of the central copper tube. This system is baked out. A suitable metal cap screws over the top of the cup and carries the thread for the bolt that exerts the pressure to close the valve. The vacuum system is thus arranged with the valves sealed to glass tube stems that lead up from cold traps and pumps through a flat, rigid, heat insulating Marinite base to the apparatus to be used, which lies in the region above the base. Over this, an insulated Marinite box can be lowered by pulleys which contain coils for heating the whole system, valves and all, to as near the softening point of the glass as it is safe to go. Once bake-out under fast pumping is accomplished and the system has cooled, the valves can be closed. Heating for 24 hours at near 450°C will suffice to give a

properly cleaned glass system that will emit gas only very slowly. The metal electrodes and parts which may be heated in experiment are outgassed at above 900°C by induction heating or electron bombardment.

The other element which was introduced followed a suggestion by W. Nottingham that the reason the earlier ionization vacuum gauges seemed to be limited to pressures above 10^{-8} mm. was that the gauges, as designed, created X-rays when the electrons used to generate the ions from the residual gas struck the grid used to accelerate them. In the older conventional design the hot wire electron emitter was at the axis with the accelerating coaxial cylindrical grid around it and a coaxial metal cylindrical ion collector outside. The electrons were accelerated between filament and grid and ionized the gas in the space between grid and collector, which with negative charge collected the ions. Ion currents measured are in proportion to gas pressure. However, as pressures decreased the gas ionization became small compared to the secondary electrons liberated from the collector plate by X-rays from the grid. These are independent of pressure. The Bayard-Alpert Gauge made the negatively charged ion collector the central wire along the axis. The grid was retained in place but increased in radius to give a large ion generating volume. The electrons were generated by two hairpin filaments outside of, but fairly close to the grid. Since the grid was positive to filaments and collector, it acted as a potential well insuring that most of the ions created within the volume reached the collector and gave an ion current proportional to the gas pressure. The linear plot of current against pressure then extended from pressures which could be measured by conventional means down to 10^{-12} mm. or less. Calibration was achieved at measureable pressures. The surface of the ion collector wire was so small that X-rays from the grid liberated negligible quantities of electrons. The gauge, however, had another property which was that of an ion pump. Once enough metal from the filament evaporation had coated the glass walls, the positive ions created between the grid and the negative filaments plus some ions that escaped capture by the wire collector were accelerated to the negatively charged metal-

coated glass walls. The glass walls, coated or uncoated, are always at nearly the same negative potential as the filaments, because of diffusion of stray electrons. The ions striking the metal deposits on the walls are absorbed. The ion gauge then acts as an ionization vacuum pump when the Alpert values are closed off and continue operating. The pumping action is sufficiently fast to maintain pressures down to about 10^{-11} mm., which equals the diffusion rate of the small amount of He gas in the room air through the glass walls, plus the slow emission of CO and other gases from the cold glass walls. The pumping action is, however, too slow to effect pressure measurements, since for the latter it need have its filament heated only a few minutes, whereas pumping requires hours. Often one gauge is used only for measurement and has so little metal on the walls that pumping is negligible, while a second one is used to pump. Bake-out removes the gas on the pump walls so that the gauge can be used again until the filaments burn out.

The ion currents are measured by a sensitive vacuum tube electrometer such as the Keithly which measures down to 10^{-15} amp., and less with the more sensitive vibration electrometer. The evacuating pumps may be ordinary mechanical pumps backing the oil or Hg diffusion pumps. For oil pumps, cold traps may not be needed if there is a roll of oxygen-free Cu in a trap in the line. The author finds that better conditions are obtained with an Hg diffusion pump and cold trap, especially if the trap is warmed and pumped out after the system has been baked for the first time. Pressures of 10^{-10} mm. can be sustained for weeks with the valves open and pumps going without using the ion gauges as pumps. Normally the best vacuum that can be obtained in Pyrex glass envelopes is about 10^{-11} mm. This limit is set by the diffusion of the small amounts of He normally present in the atmosphere through the glass wall. By placing a vacuum jacket about the tube to be evacuated, pressures less than 10^{-12} mm. can be achieved.

With pressures of 10^{-10} mm. Hg, a surface of W or Mo that has been flashed to near its melting point will require 8 hours before it is covered with a monolayer of the residual gas coming from the walls and any thin metal elec-

trodes. The formation of such a layer can be followed quantitatively by exposing a collecting metal filament surface to the ambient gas for various time intervals after flashing, then flashing to re-liberate the gas on the surface and measuring the pressure of the gas liberated after each time interval. Monolayer formation leads to an abrupt decrease in slope.

It is clear that many rapid interesting studies of surface behavior and absorption of gases are now possible. Initial studies of what happens when ions of different gases such as He, Ne, A, O_2, etc., strike different metals, how much and how they are adsorbed are now being carried out and indicate that different combinations behave quite differently. These studies allow of analysis of the troublesome factors related to time of lingering on the impact of atoms and molecules with surfaces. Data concerning the techniques involved and some results of adsorption studies will be found in the following references.

For the gauge:

Alpert, D. and Bayard, R. T., "Extension of the Low Pressure Range of the Ionization Gauge," *Rev. Sci. Instr.* Vol. 21, 571 (1950).

For the valve:

Alpert, D., *Rev. Sci. Instr.* Vol. 22, 536 (1951).

Alpert, D., "Development, Production and Measurement of High Vacua," *J. Appl. Phys.* Vol. 24, 860 (1953) and "Limiting Factors on the Attainment of Very Low Pressure," *J. Appl. Phys.* Vol. 25, 202 (1954).

Varnerin, L. J. and Carmichael, J. H., "Trapping of He Ions and the Re-emission of Trapped Atoms from Molybdenum," *J. Appl. Phys.* Vol. 28, 913 (1957).

Carmichael, J. H. and Trendelenburg, E., "Ion Induced Reemission of Noble Gases from a Ni Surface," *J. Appl. Phys.* Vol. 29, 1570 (1958).

LEONARD B. LOEB

BERKELEY, CALIFORNIA
July, 1961.

PREFACE TO THE SECOND EDITION

Between the time when the first edition was being written and the present day, the whole viewpoint of physics has undergone a revolutionary change. The year 1925 saw the termination of that era of physics which began in 1896 and which can properly be termed the *atomic period*, and the dawn of a new era ushered in by the development of the wave or *quantum mechanics*. Although the significance of this new line of approach to physical problems is not at all clear, it is certain that the attitude of the physicist toward Nature has undergone a most radical change relative to that in which the first edition of this text was written. It is, in fact, probably in those mechanical viewpoints underlying the classical kinetic theory that the strain of this change is being most felt; for it is in the molecular magnitudes lying between the electronic and the gross mechanical worlds that the seeming incongruities of classical and quantum mechanical viewpoints appear in their most striking form. It is also in this field that the classical mechanical analysis approaches exasperatingly close to the results obtained by the more precise but as yet incomplete quantum mechanical analysis. It is therefore with mixed feelings that the author has undertaken a revision of the first edition of "The Kinetic Theory of Gases." It seems, with the promise that the future holds in store, almost as if one should forego the revision of the text for some few years and then rewrite the whole story in terms of the new concepts. There is against such hesitation, however, a more immediate and practical urgency. As at the time of the writing of the first edition there is today a great need among upper-division and first-year graduate students in our American universities for ready access to the knowledge of the methods and results of the mechanical analysis of gaseous behavior. This need appears in part to have been met by the first edition of the "Kinetic Theory of Gases." As that edition was written at a time when, except for Jeans' "Dynamical Theory of Gases," there was available not a single modern text or source book on the subject, it is not

strange that in many fields, where the author had not specialized, the treatment was more classical than modern. In the meantime physics has advanced most rapidly, and the last eight years have been marked by the appearance of several excellent summaries of the subject in the German handbooks and by monographs of recent date on the rapidly developing sections of the subject. In view of the wealth of material at hand, and the changed viewpoint in the subject with the continued demand for the book, it was deemed only fitting that a revision of the book should be undertaken with a view toward modernization.

This revision has taken the form of a second edition in which at least a third of the original text has been rewritten. Needless to say the more elementary portions of the text and those dealing with classical kinetic theory have not been altered. It is chiefly those sections having to do with molecular structure and its influence on molecular behavior that have been radically altered. On this basis one will find radical changes in Chap. V on the More Accurate Equation of State, some of which have been made as a result of suggestions kindly offered by R. H. Fowler. In a similar fashion the whole of Chap. IX on Specific Heats, except the introductory section, has been reorganized and rewritten from the modern point of view with considerable extension in the application of the quantum theory to the problem. Chapter X, which was originally largely taken from Debye's excellent treatment in Marx's "Handbuch der Radiologie," has been altered in the later portions. The sections on ferromagnetism have been deleted and replaced by a section on the quantization in atomic structure as it bears on dielectric and magnetic phenomena in gases. Chapter VI on Transfer Phenomena has also been modernized in its more advanced sections through the introduction of the effects of molecular force fields on the phenomena in place of the old solid elastic impacts. Chapters VII on the Low-pressure Phenomena and XI on the Application of the Kinetic Theory to the Conduction of Electricity in Gases have been altered only to the extent of including the newer developments, certain sections, however, being rewritten. Thus, in Chap. XI, all of the section on recombination and the sections on the more complete equations for mobility had to be rewritten in the light of recent advances, while in Chap. VII the section on adsorption required rewriting. To Chap. VIII on Brownian Movements a section has been added summarizing the recent

determination of Avogadro's number, and Chap. IV on the Distribution of Velocities has had the later part enlarged to include the evaporation of molecules, the extension of the distribution law to potential fields, and a complete discussion of the recent direct proofs of the distribution law by the methods of molecular beams. It had originally been considered important to include a new chapter on molecular beams. The publication of Fraser's excellent book "Molecular Rays" makes this unnecessary, and molecular beams have been treated incidentally at several points in the text. It is hoped that with these changes the book may better continue to serve its purpose.

In closing, the author wishes to express his gratitude to Prof. R. H. Fowler for his valuable suggestions for the revision of Chap. V, to Prof. E. C. Stoner for the permission to use certain figures and tables from his excellent booklet "Magnetism," to Professors Saha and Srivastava for permission to utilize the outline of some of their excellent summaries on the application of quantization to specific heats as given in "A Text Book of Heat," in the treatment of Chap. IX; to Prof. G. P. Harnwell and Dr. J. J. Livingood for permission to include a table of electron type orbits and some of their procedure in the description of the vector model from their book "Experimental Atomic Physics"; and finally to Prof. R. T. Birge and to the American Institute of Physics for permission to include his table of physical constants in Appendix II. He is furthermore greatly indebted to Prof. K. F. Hertzfeld, who reviewed the first edition of this text, for most valuable suggestions and corrections, and to the following readers who kindly supplied him with corrections to the first edition: Prof. Bergen Davis, Dr. J. M. Eglin, Prof. H. W. Farwell, Dr. George N. Gaboury, Prof. Newton Gaines, Dr. O. M. Hovgaard, Miss Mabel Inco, Prof. O. W. Silvey, and Prof. J. A. Van den Akker. He finally desires to express his thanks to Dr. F. M. Uber for his aid in checking the equations in the text, to Mrs. Raymond C. Archibald for her invaluable assistance in preparing the manuscript, and to Lora Lane Loeb for her patience in the tedious work of reading the proof.

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May, 1934.

PREFACE TO THE FIRST EDITION

The last thirty years have seen the beginning and development of a new period in physics and chemistry, namely the atomic period. In contrast to the period preceding it where nature's processes were described in terms of continua, recent developments have emphasized the discrete structure of the submicroscopic universe. Thus, today one hears of the atoms of matter, the atoms of electricity, and even the atoms of energy, the quanta. Accordingly the modern physical sciences are demanding and constantly using atomic terminology, concepts, and methods of analysis. It is therefore important that the physicist and chemist have available a fairly complete understanding of these methods.

Of all atomic concepts, the atomic theory of matter is the oldest and perhaps the most complete. In particular because of its relative simplicity the problem of the atomic nature of gases, in the form of kinetic theory of gases, has attained the highest degree of perfection in this field. Its admirable methods of analysis are therefore indispensable not only for prospective physicists, but for both chemists and physicists engaged in experimental or teaching work.

When attempting to teach a course on the kinetic theory of gases, at the University of Chicago, in the summer of 1922, the writer discovered that there was in print but one text in the English language on modern kinetic theory. This text was far beyond the scope of the average American college student including even the first-year graduate students. The lack of facility in foreign languages among the students precluded references to texts in foreign languages. Finally, in his own field of work, which depends on the kinetic theory, the writer and his students have been much hampered by lack of a handy reference book containing a collection of the classical and more modern aspects of the kinetic theory. This book was written in an attempt to meet this situation.

The purpose of this book is, therefore, to furnish a modern text and reference book on the kinetic theory of gases for student,

teacher, and investigator in chemistry and physics. The scope of the book is to present as concisely as possible the various kinetic theory concepts and classical derivations for use by students who are beginning their third year of college work and on to the more advanced students and investigators who wish a handy reference describing more elaborately the phenomena in question. It should furnish a useful preparation to the more advanced texts and monographs on the subject including those dealing with statistical mechanics. It endeavors to develop the various concepts as independently of preceding concepts as possible, so as to avoid references to earlier chapters. Besides a simple introduction of each concept it gives derivations of three types, to wit: elementary ones, using little or no calculus; more advanced classical derivations; and in some cases the most recent developments available. It also contains the comparison of the theoretical deductions with modern experiment and a critique of the theories. Where possible the experimental methods are briefly outlined. It has the added feature of including a complete chapter giving a summary and discussion of the kinetic theory of low-pressure phenomena. A complete theoretical summary of this sort, to the writer's knowledge, has so far not been published. Finally, it contains the application of the kinetic theory methods to two more or less recent fields of research, that of dielectric and magnetic phenomena in gases and of gaseous ionization.

The writer wishes particularly to acknowledge his indebtedness to his colleague Dr. Edward Condon at whose instigation this book was undertaken. Dr. Condon originally intended to be a collaborator in this work. Lack of time prevented his doing so. The writer is indebted to him for the preparation of a large part of Chap. II, of the first two thirds of Chap. III, of the collection of the material for Chap. VI, and for some of the developments therein contained. In fact a large portion of the discussion of experimental results in Part III of Chap. VI is due to Dr. Condon's efforts.

The writer's thanks are also due to the following authors whose kindness and courtesy permitted him to use developments of some of the theories used in their texts. They are: Prof. P. Debye whose admirable treatment of dielectric and magnetic phenomena in gases in vol. 6, Theory of Electric and Magnetic Molecular Properties, of Marx's "Handbuch der Radiologie"

furnished most of the material for Chap. X; Prof. Clemens-Schaefer from whose splendid book "Einführung in die Theoretische Physik" the concise treatment of the Boltzmann derivation of the Maxwell distribution law (Chap. IV) was taken; Prof. E. Bloch for permission to use a small section of his book "Théorie Cinétique des Gaz" dealing with the proof of the Maxwell distribution law from the width of spectral lines. In this connection the courtesy of Messrs. Methuen and Company of London must be mentioned for permitting the purchase from them of the rights to make a translation.

The writer also desires to acknowledge his indebtedness for information he obtained in setting up some of the derivations and in finding useful references, to Prof. G. Jaeger for his admirable presentation of the kinetic theory in the section of Winkelmann's "Handbuch der Physik, vol. 3," and to Prof. K. Jellinek for the valuable material and references found in his "Lehrbuch der Physikalischen Chemie," including the treatment of the problem of evaporation of liquids given in Chap. VI. The latter book is a veritable gold mine of information and is notable for the completeness of the bibliography.

Finally, the writer desires to express his appreciation to Miss Velma Hutchings, without whose patient help in the preparation of the manuscript the book would have been impossible.

LEONARD B. LOEB.

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THE KINETIC THEORY OF GASES

INTRODUCTION

Scarcely thirty years ago, before the discovery of X-rays, rapid progress in physics had come to a standstill and the physicist surveyed a world in which was presented a pretty clearly defined system of nature, which could be depicted in terms of classical mechanical analogies, although the knowledge in all its details was not complete. With the discovery of Röntgen, there followed a period of feverish experimentation in which the sole aim was to gain new facts about the manifold phenomena surrounding the electron and the atom. In this search little attention was paid to a careful coordination of the new discoveries with the fundamental system of mechanics of Newton and of the times just preceding 1895.

It was about twenty-five years ago (1900) that it began to dawn on the physicists that, after all, the beautiful mechanical explanations which had stimulated so many researches, and had seemed so satisfying, were not infallible, and that such analogies too closely drawn as to the mechanism of radiation, and as to the structure of the ether, were, in fact, wrong. Today physicists seem to have come to the point of realizing that many of the observed phenomena cannot be included in the mechanical concepts of thirty years ago without a complete modification of those concepts. Such a picture as stable non-radiating electron orbits in the atom, a picture which one is inevitably forced to accept in order to correlate many of the phenomena, appears to vitiate the electrodynamics of yesterday. It is possible that a mechanism may yet be found by which such a condition is brought about, and thus the mechanical analogies may be saved—partially at least. At present, however, the trend seems to be away from all attempts at "explanation" and towards the formulation of the observed phenomena in terms of a consistent system of

relations, the correctness of which depends on being based on a few fundamental experimentally verified axioms and the proper mathematical manipulations of the equations derived from these axioms. Such formulations are seen today admirably presented in the theory of relativity and in the so-called "quantum theory." From them, given a particular situation, it is possible to predict quantitatively and definitely what phenomena will be observed in certain fields. It is thus possible to coordinate, predict, and perhaps control the phenomena by these means, but they cannot be "explained." Possibly it will in the end be the ultimate aim of science thus merely to describe, and in a measure coordinate, the physical phenomena. Perhaps the notion of the "explanation" is a mental immaturity of the past decades of science, just as the ultimate "why" which was abandoned in science in bygone years was a still greater immaturity that the human mind had to outgrow.

Be that as it may, let it for the present be assumed that the notion of the necessity of the "explanation" is an immaturity of mind. It will then be much the most satisfying mode of procedure for immature but developing (*i.e.*, growing) minds. In the world of physics there are today two types of such growing minds—those of the students who are just discovering the ideas of the last decades (and mentally living through the experiences of Joule, of Clausius, of Maxwell, and of Boltzmann), and that of the investigator baffled and puzzled by some new phenomenon. Both these types of mind have to struggle in unknown territory, both have to grasp new relations and new notions, and to both the simple expedient of concrete mechanical visualization is the most obvious course of procedure. With more maturity in the study of physics, or with a clear understanding of the new phenomenon as it is visualized, the more complete and correct formulation in some general scheme of nature may become possible, nay even necessary, because of the failure of the mechanical analogy in its details. At any rate, in the process of achieving this ultimate goal, that inspiring and stimulating method of mechanical visualization will have played its rôle. It is thus of value to the growing mind to be familiar with this mode of procedure, and in no domain of physics has the mechanical visualization had such a sweeping success as in that field termed the kinetic theory of gases. In fact, it is today perhaps the only field of physics in which the mechanical picture has not been dimmed

by the breakdown of our mechanical concepts. True it is that here and there the kinetic theory of gases borders on the peculiar mysteries of the quantum relationships, and truer it also is that the kinetic-theory concepts must constantly be modified to meet details of new discoveries. Yet today the theory stands as perhaps one of the most beautiful and satisfying pictures of physical behavior, and the analysis of new phenomena by means of its fundamental and perhaps crude concepts is now in various domains leading to valuable experimental results. So it is hoped that the student of this book will receive the same stimulus and enthusiasm from its study which inspired the writer when some years ago, as a student, he entered the field of physical research, under its spell.

Before proceeding to a consideration of the text a word of explanation will perhaps not be out of place. For the sake of simplicity, and for the purpose of appealing to the imagination of the beginning student, the agreement of the simple relations deduced with experiment and the accuracy of some of the laws cited may appear to be exaggerated. A careful scrutiny of the book as a whole should show that great care has been taken to avoid any *real misconception* without, however, killing the enthusiasm engendered by failing to emphasize a successful agreement. It must be realized that the writer is thoroughly aware of the deficiencies of the kinetic theory, although he is its ardent advocate. He regards the advance of scientific discovery and its correlating mechanical theory as a series of approximations to the true sequence of phenomena. What, for example, was a great triumph of yesterday in accounting for the coefficient of viscosity of a gas by an expression $\eta = \frac{1}{3} N m \bar{c}^2$ is today, on the kinetic theory but a crude approximation which neglects the present view of molecules whose apparent average diameter determined by intermolecular force fields is necessarily a function of their average velocity. Doubtless in years to come the successful and beautiful treatment by Chapman will, in its turn, be but a second-order approximation to an even more complicated and more precise series of relationships. Such improvements are, nevertheless, continual advances rather than revolutionary changes. Thus, imperfect as the theory may be today, it is an advance over previous concepts and for practical purposes may be of incalculable value. It is the endeavor in this book to

avoid confusing the student at the outset with a statement of all the complexities encountered in more modern work. Accordingly, the theory will be logically developed from the simplest conceptions. As, with increasing knowledge of the facts, the discrepancies begin to appear to the student, the weaknesses of the theory will be carefully pointed out. Then in later chapters, when the mind is ready for them, detailed descriptions of the difficulties and of the way in which the theory attempts to meet them will be given. It is felt that in *this way only* can the best aims of the student be served. The reader is, therefore, warned that before he accept a simple assertion as the complete, accurate, and final statement of a law he would do well to consult the index for references to a more complete discussion in a later and more appropriate chapter. In some cases the attention of the reader will be specifically called to such discussions in the text. With this caution the reader may open the book and discover for himself the fascinating romance of the eternal motions of the myriads of minute solar systems called molecules which constitute that state of matter which is termed the gaseous state.

CHAPTER I

HISTORICAL*

Age of Philosophical Speculation.—Nearly 2300 years ago (400 B.C.) the Greek philosophers Leucippus, Democritus, and their pupils pictured a world made out of minute particles or atoms which were in constant motion. Later (95 B.C.), Lucretius,[1] who was familiar with the earlier writings, pictured gases somewhat as they are pictured today.† However true these philosophic speculations may seem today, they were then no more than wild guesses. Many another philosopher of that time fitted gases into his scheme of nature in a very different manner. As these pictures were not in accord with later discovery, they were ignored and forgotten. It is, then, because the fortunate coincidence that a speculation made 2300 years ago happens to agree with an experimental fact of today that a group of persons frequently assert that there is nothing new in the world, and that the more modern atomic theory was discovered by the Greeks. This, of course, is absurd.

Birth of an Hypothesis.—The kinetic theory of gases could not have been legitimately propounded as a theory with any semblance of reality until the nature of heat was known, and until the relationship of heat to work and energy had been established.[2] During the period 1760 to 1800 the views of Black[3] the advocate of the caloric theory of heat, still held the scientific stage, whence they had evolved from the first measurements on quantity of heat. From then on until 1850 the famous experiments of Rumford and Joule[3] on the relation between heat and work were in progress, so that by 1856 the time was ripe for the two independent papers of Krönig and of R. Clausius (1857), in which

* Throughout this book numbered references are to references at the close of each chapter.

† The famous poem "*De Natura Rerum*," in which this scheme is propounded, is well worth reading. It appears in Everyman's edition. In reading it, it is to be noticed that the scheme of nature devised is a logical deduction based on certain crudely observed phenomenon, such as the conservation of matter. (Book I, lines 146–328.)

the kinetic theory of gases was proposed and based on an experimental footing.

Before these two definite enunciations of the theory there had been earlier attempts, none of which were complete enough to be included with them. In fact, Clausius admits to having been familiar with a paper of Joule's published in 1851, in which Joule computed the gas pressure on the basis of the heat motions of the gas molecules. There was an article of a similar nature by a practically unknown physicist Herapath, in 1821. Credit must also be given to the mathematical physicist and genius Daniel Bernoulli, for in his then little known "Hydrodynamics," published in 1738, he had built up a correct and very complete kinetic theory of gases. He had at that time no experimental basis for his assumptions, and accordingly his theory must be classed among the philosophic speculations.

Establishment of an Hypothesis.—The deductions of Clausius were of sufficient accuracy and completeness so that his paper attracted widespread attention, and such master minds as Maxwell[4] and Kelvin were stimulated to interest themselves in the theory from 1860 to 1880. In later years Boltzmann,[5] O. E. Meyer,[6] Jaeger,[7] Jeans,[8] Knudsen,[9] Chapman, Enskog, Sutherland,[18] and others have also contributed a considerable amount. The theory as it was left by Maxwell, Kelvin, and Boltzmann, however, remained no more than an hypothesis, for, in spite of many quantitative agreements between the theory and the behavior of gases, no proof of the separate existence of the atoms and molecules had been obtained, nor had any observations been made that could really demonstrate the continual heat motions of the molecules.[10] This left the kinetic theory a very successful and interesting analogy, but that was all.

Retarded Development. School of Energetics.—From 1890 to 1908 the theory suffered a retarded development due to the violent attacks on it by Wilhelm Ostwald and his school of "Energetics."[11,12,13] This was at a period when thermodynamics had been found to be a very useful tool of the physicist and chemist. At that time, perhaps somewhat as with Relativity today, the physicists sought to solve all the problems of the universe by thermodynamics. Now thermodynamical reasoning does not require a knowledge of the precise mechanism of a reaction for its applications. All that is required is a complete knowledge of the energy and heat relations of a cycle of opera-

tions. Ostwald, accordingly, argued that with the thermodynamical treatment of a process one knew all that there was essential to be known about the process and that further mechanical assumptions as to the mechanism of the reactions were gratuitous hypotheses. He was correct in asserting that the mechanical assumptions of the kinetic theory were unproved hypotheses. He was, however, wrong in urging that the rather sterile thermodynamical reasoning be substituted for the neat and stimulating analysis of the kinetic theory, for, strangely enough, science progresses chiefly by the mechanical analogies of nature's processes which occur to the mind of the investigator. And the kinetic theory is just such a mechanical analogy. In fact, it seems to be the very fallibility of such mechanical pictures which makes experimental test imperative and hence leads to further investigations and clearer knowledge. Science cannot progress much through the manipulations of equations indicating only the heat and energy transfers in a reaction, for such manipulations do not generally suggest further experiments.

Birth of a Theory.—Fortunately, these attacks were brought to an abrupt end through the brilliant experiments of Jean Perrin[14] in France in 1908. Perrin succeeded in quantitatively demonstrating the existence of the continual heat motions of the molecules of a liquid by a study of the Brownian movements of suspended particles. These proofs, as will later be seen, were of such a definite nature that even Ostwald accepted them and relinquished his exclusive claims for "energetics." Later, these results were extended to gases with a far higher degree of accuracy through the beautiful oil-drop experiments of R. A. Millikan.[15]

Later Development.—The final developments in the kinetic theory of gases, upon which the closing chapters have not yet been written, were due to the new methods of study opened up by the discovery of X-rays in 1895. The X-rays led to a study of the carriers of electricity in gases, the ions and electrons.[16] Now it has been shown that the ions are charged molecules or groups of molecules of the gases, and the electrons act as essentially mathematical point charges from the point of view of the kinetic theory.[16,17] Their electrical charges enable the ions and electrons to be singled out from the other molecules, and thus permit their properties to be studied after encountering the other gas molecules under varying circumstances. The result is that the

kinetic theory of gases has made much progress in the able hands of Langevin and Lenard, J. J. Thomson, Franck, Townsend, and Compton,[19] through the additions which have come to it from the theory of the gaseous ions.

Today, then, the kinetic theory of gases can be regarded as being far beyond the speculative philosophy of the Greeks, and far beyond the kinetic hypothesis of Clausius and Maxwell. In fact, it is as well-established a theory (that is, a close-working mechanical analogy to the real processes) as any theory which is accepted by science.

Wave Mechanics.—Since the first edition of this book was written, two new aspects of nature bearing on the history of the kinetic theory have been developed extensively. The first of these was the partial clarification of the difficulties raised by the quantum laws in atomic physics through the development of the wave or quantum mechanics by L. de Broglie, Schroedinger, Pauli, Heisenberg, Born, and Dirac in the period from 1925 to 1930. To this development we owe the dualistic conception of matter and energy (*i.e.*, the light wave and the light corpuscle or photon—the particulate electron and the wave-packet electron), the statistical relations between these apparently contradictory aspects, and the principle of indeterminacy or uncertainty principle of Heisenberg. All these developments, while drawing heavily from the methods of the kinetic theory in their analyses, are in principle and viewpoint opposed to the foundations on which the kinetic theory rests, to wit, the Newtonian mechanics. It was of course vain to hope that being assemblages of electrons and protons, the atoms and molecules would fail to exhibit the dualistic properties of their constituents so that the classical viewpoint could be retained intact for atoms and molecules. The necessity of a direct test of the expected dual behavior of matter as applied to the supposedly corpuscular atoms and molecules was thus obvious. It came in 1929 as a result of the technique used in the second new development of kinetic theory, the method of molecular beams. The method grew out of Dunnoyer's[20] pioneer work in 1911 and was developed in part by Wood, Eldridge, Langmuir, Cockcroft, Ellett, Johnson, though largely by Otto Stern and his associates beginning in 1921. Using molecular beams of He and H_2 gases, first with a velocity distribution and later with a more or less homogeneous group of velocities, Stern and Knauer, and later Stern and

Estermann, succeeded in diffracting these beams from the crossed grating lattice of the surfaces of NaCl and NaF crystals as if they were waves of length λ given by the de Broglie law $\lambda = h/mv$. In this equation h is the Planck constant, m the mass of the atoms or molecules, and v their velocity. The precision of the technique was such that these measurements verified the equation to within 2 per cent, which to date gives the most complete and accurate experimental verification of the de Broglie law.

It thus turned out that the newest technique of the experimentalist, the method of the molecular beam, which gave the most direct and convincing proof of the correctness of the kinetic interpretation of matter, was also the method which demonstrated clearly the defects in the classical kinetic theory. The proof of the dual nature of atoms and molecules is so definite that it must be accepted as fact. It accordingly becomes necessary to assume that the particulate concept of the atoms and the molecules, so essential to the kinetic theory of the past, *is but one aspect* of a very much more general and complicated entity which at present can only be described by equations and cannot be expressed in any mechanical picture. This fact does not invalidate or contradict any portion of the kinetic theory. It only shows that as regards the correct interpretation of molecular behavior, the kinetic theory is an excellent approximation to *one* aspect of the problem. It places in the future the fascinating problem of developing the more complete and accurate description of the concepts of the atoms and molecules. In fact, even this early, successful attempts have been made at deriving some of the laws of molecular or atomic impacts by means of the wave mechanics so that one can feel certain that the new approach is capable of giving important results in this field.[22]

Despite its apparent incompleteness and the fact that it is but an approximation, the kinetic theory nevertheless furnishes much valuable information for the present and offers invaluable tools for future analyses. It will always remain as one phase of the description of matter and as the foundation for future development.

References

1. Lucretius: "The Nature of Things," Book II, lines 62–332, Everyman's Library, J. M. Dent and Sons, New York.

2. Lucretius: *Loc. cit.*, Chap. II, Secs. 1, 5, 8.
3. Mach, E.: "Principien der Wärmelehre," p. 156, Johann Ambrosius Barth, Leipzig, 1896.
4. Maxwell, James Clerk: "Scientific Papers," edited by W. D. Niven, Cambridge University Press, Cambridge, 1890.
5. Boltzmann, Ludwig: "Vorlesungen über die Gas Theorie," Johann Ambrosius Barth, Leipzig, 1910.
6. Meyer, O. E.: "Kinetic Theory of Gases," translated and revised by R. E. Baynes, Longmans, Green & Co., London, 1899.
7. Jaeger, G.: "Fortschritte der Kinetischen Gas Theorie," F. Vieweg und Sohn, Braunschweig, 1919.
8. Jeans, J. H.: "Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1921. (Dover Reprint)
9. See Chap. VII, Secs. 77–82 inclusive for references to Knudsen's work.
10. Ostwald, W.: "Vorlesungen über Naturphilosophie," 2d ed., pp. 162–201 (ninth lecture), Veit & Co., Leipzig, 1902.
11. Perrin, J.: "Atoms," p. i of Preface, translated by D. L. Hammick, Constable & Co., London, 1920.
12. Morgan, J. L. R.: "Elements of Physical Chemistry," introductory remarks, Sec. 3, p. 3, John Wiley & Sons, Inc., New York, 1911.
13. Ostwald, W.: "Grundlinien der Anorganischen Chemie," see p. 153, W. Engelmann, Leipzig, 1900.
14. Perrin, J.: *Loc. cit.*
15. Millikan, R. A.: "The Electron," Chap. VII, University of Chicago Press, Chicago, 1917.
16. Thomson, J. J.: "Conduction of Electricity through Gases," Cambridge University Press, Cambridge, 1906. Crowther, J. A.: "Ions, Electrons and Ionising Radiations," Edward Arnold & Co., London, 1924.
17. See Chap. XI, Sec. 102.
18. For work of Chapman, Enskog, and Sutherland see Chap. VI, Secs. 62–64, and 69.
19. For references to this work see all of Chap. XI.
20. Dunnoyer: *Compt. Rend.*, **152**, 594, 1911.
21. Knauer and Stern: Z. Physik, **53**, 779, 1929. Estermann and Stern: *Z. Physik*, **61**, 95, 1931. Estermann, Frisch, and Stern: *Z. Physik*, **73**, 348, 1931.
22. Knauer, F.: Scattering of Molecular Beams in Gases, I, *Z. Physik*, **80**, 80, 1933. Massey and Mohr: Theoretical Scattering of He Atoms in He, *Nature*, **130**, 276, 1932.

Books Recommended

a. For historical outline of the development of the concepts of heat, Mach: *loc. cit.*

b. Lucretius: *Loc. cit.*

c. Historical Sketch and the Introduction to Jeans: "Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1911.

CHAPTER II

THE MECHANICAL PICTURE OF A PERFECT GAS

1. The Mechanical Equivalent and the Kinetic Hypothesis. In the historical outline it was stated that there could be no proper justification of the kinetic-theory hypothesis until the relation between heat and work had been established. It is now necessary to show why this was so. It will be seen that it was not strange that Joule, one of the first to establish the relation between mechanical work and heat, should also have been one of the first to try to formulate a kinetic theory of gases.

When a gas like helium is heated in an enclosed vessel so that it cannot expand, two things occur: first, it absorbs a given quantity of heat per unit mass, and, second, its temperature rises. This heat is stored in the gas in some form and is given out again on cooling. Furthermore, in absorbing the heat there is no appreciable change in the gas except the increase in temperature and an increase in pressure. This pressure increase in the gas is what would cause the gas to expand and do work corresponding, in the ideal case, to the heat put in. The question then arises as to how the gas can absorb heat and increase its pressure.

Assistance is derived in understanding this phenomenon by inquiring into the meaning of temperature, and as to how the temperature is related to the pressure. The experiments of Boyle, in 1662, showed that for a given temperature the relation between pressure and volume of a gas was given by the relation $pv =$ constant, where p is the pressure and v the volume. Later, Charles, Mariotte, and Gay-Lussac studied the behavior of gases at constant volume and constant pressure as the temperature was increased. It was found that at constant volume an increase in temperature of $\Theta°$ gave a change in pressure represented by the equation

$$p = p_o(1 + A\Theta),$$

in which p is the pressure at the temperature Θ and p_o is the pressure at 0° on the thermometric scale used. If v_o is the constant volume of the gas, the equation may also be written as

$$pv_o = p_o v_o(1 + A\Theta).$$

In virtue of Boyle's law, the left-hand side of the equation is constant and will remain the same even if v_o be changed to some new value v. Hence it is possible to write

$$pv = p_o v_o(1 + A\Theta).$$

If to p on the left-hand side the value p_o be assigned, the expression

$$v = v_o(1 + A\Theta), \text{ readily follows.}$$

This is the law for the change of volume with temperature which was discovered experimentally. Experimentally, it does not hold accurately for any gases, for the constant A in the pressure equation differs from that in the volume equation (see Secs. 48 and 51). It is approached more accurately by the gases that are furthest from their condensation temperature. For such gases the A is nearly the same and the condition in which this is so can be called the limiting state to which all gases strive the farther they are removed from their condensation temperatures. Strictly, it is only a limiting case, and a gas obeying this law is defined as an ideal gas. Elementary treatments of the kinetic theory which will be derived in this chapter deal with such gases.

If it be assumed that both equations hold and that A is the same for pressure and volume changes, one can proceed to use the common equation

$$pv = p_o v_o(1 + A\Theta).$$

Factoring A out of the parenthesis, the equation becomes

$$pv = p_o v_o A\left(\frac{1}{A} + \Theta\right).$$

This equation gives a new insight into the process of expansion, for if $\Theta = -1/A$, $pv = 0$, that is, at $-1/A$ either p, v, or both are 0. Since Θ is a temperature, $1/A$ is a temperature, and it is the temperature which, if attained below the zero from which Θ is measured, would make pv equal to zero. Thus, since A is a universal constant for the expansion of an ideal gas, $-1/A$ gives a new definition of zero on an absolute scale. That is, $(1/A)°$ below the zero from which Θ is measured is the absolute zero of temperature at which a gas exerts no pressure. On this basis $1/A + \Theta$ may be replaced by T, calling T the *absolute temperature*. If the constant quantity $p_o v_o A = R$, be written with the understanding that v_o corresponds to the volume of 1 gram-molecule of the gas, the *equation of state* for an ideal or perfect gas is given by

$$pv = RT.$$

This equation will at once aid in understanding the nature of temperature.* Its interpretation is aided by means of dimensional analysis of the left-hand side of the equation. Pressure is the ratio of a force to an area, that is, it is a force divided by the square of length. Volume is the cube of a length. The product pv has thus the dimensions of a force times a length. But, dimensionally, force times a distance represents work done or energy.† Thus RT is dimensionally a work or an energy, and as T increases the product RT increases in proportion, and hence the energy that is represented by pv in the gas increases. That is, RT is proportional to an energy that goes into the gas as it is heated, and T is a measure of this energy. When T is 0 then the energy is 0. Now for constant volume p is also increased in proportion to the increase in energy and the key to an interpretation of the

* A moment's reflection shows that temperature is entirely different from the other measurable quantities of physics. The important stages in the development of the concept of temperature cannot be overemphasized.

The notion of temperature has its origin in our sense perceptions of warmth and coldness. The sensations of an individual are far too relative and crude to serve as a working basis for temperature measurements, and so physical means have been developed for the purpose, which are independent of the thermal perceptions of the observer. These are based usually upon the recognition by the observer of changes in some property of a substance, known as the thermometric substance, which is placed in the space of which the temperature is desired to be known (*e.g.*, the expansion of liquids, etc. which give a purely empirical scale).

The utility of the temperature concept in physics is twofold. In the first place, the assignment of numbers representing the temperatures of a set of bodies makes it possible to determine in what direction heat will flow between the bodies if any of them are placed in thermal contact. This use is embodied in the statement that heat flows from bodies of higher to bodies of lower temperature. Obviously, however, for this purpose any scale of temperature suffices so long as larger numbers are always assigned to warmer bodies. The other functions of the temperature concept are developed in the study of thermodynamics and are concerned with the rôle played by temperature in conditioning the efficiency of all processes which are designed to transform heat into mechanical work.

It is this second property of temperature which serves to define the absolute temperature scale. Rigorously, the absolute temperature scale is to be regarded as derived from the second law of thermodynamics. The justification for the approach to the subject given in the preceding paragraph lies in its historical correctness, and, further, in the fact that the perfect gas thermometer is the actual experimental mode of establishing the absolute temperature scale.

† Force times distance may also represent a torque, but as this does not enter into considerations such as these it need not be discussed here.

phenomenon lies in *finding a mechanism* by which both the pressure of the gas and its internal energy are simultaneously increased in proportion.

This was solved by Joule by the assumption that a gas was made up of molecules, or particles in constant motion. Such particles striking a solid wall and rebounding from it elastically will transfer momentum to it. The rate of momentum transfer to the wall gives the force exerted by the particles on the wall and represents the pressure. If the pressure be calculated, as will be done in Sec. 5, it will be seen that it depends in a simple way on the kinetic energy of the gas molecules. Thus the energy represented by the quantity RT is related to the kinetic energy of motion of the molecules, while the pressure is also a consequence of this. This picture requires, however, that a simple relation exists between heat and mechanical energy or work. The idea underlying this concept is that, in a gas, heat is nothing else than the kinetic or mechanical energy of motion of the gas molecules, so that, in expanding, a gas does work at the expense of the kinetic energy of its molecules, which represents its heat energy.

The assumptions made by Joule, of the molecular nature of the gas, and which form one phase of this picture, were not as novel at the time as might be gathered from this discussion, for as will be seen in Sec. 8, the molecular nature of a gas had been pretty well foreshadowed by Avogadro in attempting to account for the laws of chemical combination of gases. Thus, the contribution of Joule lay in associating the heat taken up by the gas with the increase in kinetic energy of its molecules, and showing that this also gave the required pressure change. With such an introduction it is possible to proceed to set forth a group of assumptions about the molecules and their motions which will enable further analysis to be carried on. As will be seen, these assumptions apply to an ideal gas. They do not conform to reality. They, however, sufficiently simplify the problem to make it possible to proceed with an elementary analysis. As the understanding of the processes advances, it will become possible to alter the simple assumptions to conform to the real gases.

2. The Numerical Value of RT.—It is worth while before proceeding further to obtain a numerical value for R, the universal gas constant. This may be calculated as follows: A gram-molecule of gas at 0°C. and 760 mm of Hg (1 atmosphere of

pressure) occupies a volume of 22,410 cm³.* The value of A, evaluated with respect to 0°C., is given by experiment as 0.003665. Since by the above R is given as

$$R = p_o v_o A,$$

then $R = 1 \times 22{,}410 \times 0.003665$ cm³ atmospheres per degree
$= 82.07$ cm³ atmospheres per degree.

The cm³ atmosphere is a rather awkward unit of energy. More common ones are the absolute c.g.s. unit, the erg, or the classical heat unit, the calorie. Making use of the density of mercury and the value of gravity the relation follows:

$$1 \text{ atmosphere} = 1{,}013{,}300 \text{ dynes per cm}^2.$$

Choosing as the definition of the calorie the amount of heat required to raise 1 gram of water from 15 to 16°, the value of the mechanical equivalent of heat is

$$1 \text{ cal.} = 4.182 \times 10^7 \text{ ergs.}$$

In view of these results the value of R can be given in mechanical or in heat units as follows:

$R = 82.07 \times 1.0133 \times 10^6$ cm³ dynes per cm² per degree
$= 8.316 \times 10^7$ ergs per degree
$= 1.988$ cal. per degree.

3. The Model of a Perfect Gas.—In order to carry on the analysis, the following simplified picture of a gas must be made. The gas is to be considered as an assemblage of particles called molecules which move freely in the space occupied by the gas, colliding with each other and with the walls of the vessel. The assumptions upon which the mechanical picture of a gas is founded, and which are introduced in this chapter and elaborated and modified in the following chapters may be enumerated as follows:

1. A gas consists of particles called molecules which in a stable state and in a given type of gas are all alike. The mass of the molecules will be denoted by m.

2. The molecules are in motion, and as they are material bodies Newton's laws of motion may presumably be applied.

3. The molecules behave as elastic spheres of diameter σ. In perfect gases the number of molecules in the space considered is small enough so that the mean distance between the molecules

* The conditions denoted here of 0°C. and 760 mm of Hg will be designated as N.T.P. hereafter, meaning Normal Temperature and Pressure.

is large compared to their diameter, and thus for these elementary considerations the space they occupy may be disregarded.

4. In perfect gases no appreciable forces of attraction or repulsion are exerted by the molecules on each other or on the substance of the containing vessel.

(1) The reasons for the assumption of the molecular nature of the gas have been introduced in Sec. 1. The assumptions of the stable state and similarity of the molecules are introduced to simplify the initial calculations.

(2) That the molecules are endowed with motions follows from the fact that they are assumed to have kinetic energies of agitation and are reflected from the walls, producing pressure. That they obey Newton's laws is a consequence of the assumption that they are material bodies in motion, and Newton's laws are assumed applicable to all material bodies.

(3) The assumption of perfect elasticity is necessary in order to account for the reversibility of the absorption and emission of heat. It is an essential assumption if the correct relation between heat and work is to be maintained for the ideal gas, for if it be assumed that they are not elastic, kinetic energy gained on heating would go into the deformation of the atoms when inelastic impacts took place. Unless this energy could be given back on cooling, heat would be lost on heating and cooling, or if the kinetic energy were converted into work after heating, less work would be obtained than was put in and the relation between heat and work would not be fulfilled. Actually, in some gases that are chemically reactive, like Cl_2 and Br_2, this elasticity does not hold and energy goes to atomic deformation, which may be radiated away as electromagnetic radiation, as is shown in Chap. IX. In general, the assumption of elastic impacts is, however, justified. The assumption of point molecules is a simplifying assumption which corresponds to reality only as a rough approximation. The consequence of the finite size of the molecules is seen in Chap. III.

(4) Gravitational forces do undoubtedly act between the molecules. These forces are exceedingly minute. The force of gravitation between two bodies of equal mass m is given by $f = G\frac{m^2}{r^2}$, where r is the distance between them and G is the constant of gravitation. This force f is $6.658 \times 10^{-8}\ m^2/r^2$ dyne, if m be in grams and r in cm. Since m is of the order of 10^{-24} gram

for the H_2 molecules and r is of the order of 10^{-8} cm when the molecules are in contact, the force is minute indeed. A better idea can be gained of the influence of these forces if the kinetic energy of the molecules at 0°C. is compared, which by Sec. 11 is about 5×10^{-14} erg, with the gravitational potential at contact between molecules, which is of the order of $6 \times 10^{-8} \times 10^{-48}/10^{-8}$ or 10^{-48} erg for two H_2 molecules. The *intermolecular forces of attraction* are, however, much greater and their potential energies at molecular contact become comparable to the kinetic energies of agitation near the condensation temperatures. For ideal or perfect gases they may for simplicity be neglected. Their influence, however, is measured for real gases by the term a/v^2 in the Van der Waals' equation studied in Chap. V.

4. Molecular Motions.—Preparatory to their use in later developments a statement of Newton's laws of motion will here be given. These are fundamental to the classical mechanics on which the kinetic theory is based:

1. A body continues in its state of rest, or of straight uniform motion, except in so far as it is compelled to alter that state by impressed force.

2. Change of motion is proportional to the impressed motive force, and takes place in the direction in which that force is impressed.

3. Reaction is always equal and opposite to action, that is, the mutual actions of two bodies are always equal and take place in opposite directions.

The statement of the laws is included here mainly for reference purposes. Mathematically, the position of a particle is determined relative to a Cartesian coordinate system by its coordinates x, y, z, which give its position at the time t. The velocity components are then dx/dt, dy/dt, and dz/dt and the momentum is defined as having the components mdx/dt, mdy/dt, mdz/dt. As the components of the force are F_x, F_y, F_z, the second law yields the equations

$$F_x = \frac{d}{dt}\left(m\frac{dx}{dt}\right); F_y = \frac{d}{dt}\left(m\frac{dy}{dt}\right); F_z = \frac{d}{dt}\left(m\frac{dz}{dt}\right).$$

The kinetic theory has frequently to deal with assumed perfectly elastic collisions between individual molecules and between a molecule and a wall. The study of elastic collisions as governed by Newton's laws of motion is greatly facilitated by the use of

two principles, which are mathematical consequences of Newton's laws, the conservation of kinetic energy and of momentum in the collision. In an elastic collision:

1. The sum of the kinetic energies of the colliding bodies before impact is equal to the sum after impact.

2. The sum of the momenta of the two bodies before impact is equal to the sum after impact.

A simple application of these principles, the result of which will be needed later, is to the case of the elastic impact of a spherical ball striking a wall at normal incidence. Let m, v_1, v_2 be the mass and initial and final velocities of the ball, and M, V_1, V_2 these same quantities for the wall. Then

$$\frac{1}{2}mv_1^2 + \frac{1}{2}MV_1^2 = \frac{1}{2}mv_2^2 + \frac{1}{2}MV_2^2$$

and $$mv_1 + MV_1 = mv_2 + MV_2,$$

so that $$m(v_1^2 - v_2^2) = M(V_2^2 - V_1^2).$$

Dividing these by $$m(v_1 - v_2) = M(V_2 - V_1),$$

$$v_2 + v_1 = V_2 + V_1.$$

If the wall be immovable, then $V_2 + V_1 = 0$, so that

$$v_2 = -v_1,$$

i.e., the ball rebounds with the same velocity as that with which it struck the wall. The total change of momentum of the ball is $2mv$, where v is now the common velocity before and after impact. This is also the impulse communicated to the wall.

5. The Kinetic Interpretation of Gas Pressure.—In this section will be given an extremely simple mechanical deduction

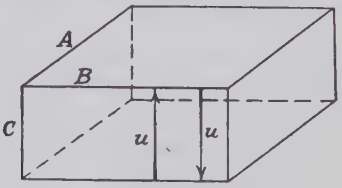

FIG. 1.

of the equation of state, substantially as it was first given by Joule in 1851.

The ν molecules of the gas are contained in a rectangular box of edges A, B, and C (Fig. 1). It is supposed that there is no actual streaming, or body motion, of the gas, the motions of the molecules being perfectly chaotic. Let u be the mean speed of the molecules, and for simplicity's sake let it be supposed that they

all move at the same speed. Owing to the random nature of the motions it may be supposed that the motions are equivalent to a situation in which one-third of the molecules are moving parallel to the length, one-third parallel to the breadth, and one-third parallel to the depth of the box.*

Every time a molecule collides with a wall its direction of motion will be reversed (Sec. 4), and so its change of momentum will be $2mu$. In 1 second a molecule which is traveling parallel to an edge of length C will traverse the length of the vessel u/C times, and so will collide with each of the end walls $u/2C$ times per second. As one-third of the molecules are moving this way, the number of collisions per second on an end wall is $u\nu/6C$, where ν is the number of molecules in ABC. Thus the total change of molecular momentum per second by an end wall of area AB is

$$2mu \times \frac{u\nu}{6C} = \frac{\nu mu^2}{3C}.$$

But by the second law of motion this rate of change of momentum of the molecules is equal to the total force exerted upon them. By the third law this is also the force which they exert on the wall. The pressure on the wall is equal to this force divided by the area, so that

$$p = \frac{1}{3}\frac{\nu mu^2}{ABC}$$

or

$$pv = \frac{1}{3}\nu mu^2 = \frac{2}{3}\left(\frac{1}{2}\nu mu^2\right) = \frac{2}{3}E.$$

This equation makes it evident that the value of pv is simply two-thirds of the total kinetic energy E of the molecules. Comparison with the equation of state shows how the temperature of the gas is simply proportional to the total kinetic energy of the molecules of the gas.

6. Work of Compressing a Gas.—An instructive picture of the way in which mechanical work done on a gas is transformed into

* This apparently natural assumption is one which has a very great significance in the kinetic theory, as will be seen in Sec. 91 of Chap. IX. It assumes that if the molecules are great in number and have random motions the velocities and hence kinetic energies are equally distributed among the three degrees of freedom of motion along the three coordinate axes. It is, in fact, an application of the theorem of equipartition of energy to the degrees of freedom of motion in a gas, to be discussed in Chap. IX.

thermal energy of the molecules is obtained by a simple extension of the analysis of the preceding section.

The experimental fact to be explained is that a gas is warmed when it is compressed adiabatically (*i.e.*, without loss of heat through the walls of the container) and, conversely, is cooled when it expands adiabatically.

Suppose the gas to be contained in a cylinder which is equipped with a piston which moves without friction in the cylinder. If A is the area of the piston, then pA will be the force which the gas will exert tending to drive the piston outward. Hence pA is also the force which must be exerted by some external agency to maintain the piston in equilibrium. If a greater force be exerted by this external agency, the piston will move inward, or if a lesser force be exerted, it will move outward.

It is interesting to consider the effect on the molecular motions of steadily pushing the piston in at a speed of α cm/sec. It will be supposed that this speed is small compared to the molecular motions, so that no actual streaming of the gas is set up. If C is the length of the cylinder the number of collisions per second on the moving piston will be $u\nu/6C$ as before. But now the molecules are striking a moving wall and the effect is different from that of the preceding section on this account.

The simplest way to see the effect of the piston's motion is the following: Consider how a collision of a molecule with the wall would appear to a person riding along with the piston. The molecule approaches him with a speed $u + \alpha$ and leaves him with the same speed after the collision with the wall. But to leave the piston with a speed $u + \alpha$ relative to it means to move relatively to the cylinder with a speed $u + 2\alpha$.

The change in kinetic energy at each collision is an increase of amount:

$$\frac{1}{2}m(u + 2\alpha)^2 - \frac{1}{2}mu^2 = 2mu\alpha + 2m\alpha^2 = 2mu\alpha\left(1 + \frac{\alpha}{u}\right).$$

Since by hypothesis α/u is small, it may be neglected. Multiplying by the number of collisions per second, an expression is obtained for the amount of kinetic energy imparted to the molecules by the piston in a second:

$$\frac{1}{3}\frac{m\nu u^2}{C}\alpha = \frac{pv}{C}\alpha = pA\alpha.$$

In a small time dt piston will move a distance αdt and the volume of the gas will be changed by $dv = A\alpha dt$. In this time the energy imparted to the molecules will be

$$pA\alpha dt = pdv.$$

It is thus seen that when a gas is compressed adiabatically by a *slowly moving* piston the work done goes into increasing the energy of the molecular motions, the amount of work thus done being simply equal to the product of the pressure which the gas would exert on a stationary piston at each successive position by the change in volume. It is evident that all that has been said applies equally well when the piston is moved slowly outward—in this case the molecules communicate energy to the wall at the same rate pdv, and the gas is thereby cooled.

7. Irreversible Compression.—Students of thermodynamics are already familiar with the important distinction in that subject between reversible and irreversible processes. Reversible processes, such as the reversible compression or expansion of a gas, must be carried out in such a way that the forces are in equilibrium at all stages of the process and as a result all the motions occur with infinite slowness. If the processes be irreversible, it is shown in thermodynamics that there is always an attendant degradation of energy from the "perfectly available" mechanical energy to the thermal energy of "limited availability."

The discussion of adiabatic compression of a gas, given in Sec. 6, admits of an illuminating extension to show the mechanical picture of the distinction between reversible and irreversible processes. In considering the communication of energy to the walls by the molecules, it was supposed that α was so small that α/u was negligible. This is the case in the infinitely slow reversible processes. If α/u is not negligible, then it is evident that the accurate expression for the energy exchange between the piston and the molecules in time dt is

$$\frac{1}{3}\frac{mvu^2\alpha}{C}\left(1+\frac{\alpha}{u}\right)dt.$$

If P is the pressure exerted by the gas against the *moving* piston, then in time dt the force PA will have acted through the distance αdt so the work done by the piston will be

$$PA\alpha dt = Pdv.$$

Returning to the accurate expression for energy exchange, this may be written as

$$\frac{pv}{C}\alpha\left(1+\frac{\alpha}{u}\right)dt = p\left(1+\frac{\alpha}{u}\right)dv$$

as the amount of energy communicated to the molecules in the volume change dv. Equating the two expressions in virtue of the law of conservation of energy and dividing by dv:

$$P = p\left(1+\frac{\alpha}{u}\right).$$

This indicates that the *actual pressure P which a gas exerts when it is being compressed is greater than the statical pressure p which it would exert against a stationary wall at the corresponding stages of the compression.* Similarly, *during expansion (α is negative) the actual pressure P is less than the statical pressure p.*

The obvious result of these conclusions is that if a gas be compressed at a finite velocity and then expanded to its original volume, all of the work of compression will not be regained on expansion and so the gas will be left warmer than it originally was. Thus the simple kinetic picture clearly portrays a conclusion gained in thermodynamics by rather abstruse reasoning.

8. Avogadro's Rule.—In Secs. 1 and 2 the experimental fact that R has the same numerical value for all gases when a mol (*i.e.*, a gram molecule) of the gas is considered has already been presented. This important result calls for more extended discussion.

The concept of molecular weight as used thus far is a conclusion derived originally from the quantitative experimental laws of chemical combination. After Lavoisier, in 1774, had enunciated the law of conservation of mass in chemical reactions the next great step was the formulation by Richter and Proust of the law of definite proportions: *A definite chemical compound always contains the same elements united in the same proportion by weight.*

It was then possible to ascertain the relative combining weights of the various chemical elements. Thus if the combining weight of hydrogen were taken as unity, experiment showed that the combining weights of chlorine, oxygen, and sulphur were 35.5, 8, and 16 respectively. On the basis of the atomic theory these numbers mean, respectively, the weights of the atoms of chlorine, oxygen, and sulphur which combine with one atom of hydrogen when the weight of the hydrogen atom is taken as the unit. But it is important to notice that we are not entitled to conclude from these data alone that these numbers represent the relative weights respectively, of single atoms of chlorine, oxygen, or sulphur.

This will be true only in case a single atom of these elements enters into combination with hydrogen in the compound from which the combining weights were determined.

This work was followed by the publication in 1808 by John Dalton of the *law of multiple proportions,* which says that: *When two elements unite in more than one proportion, for a fixed mass of one element the masses of the other element bear to each other a simple ratio.* Dalton further gave a brilliant explanation of these laws on the basis of his atomic theory as presented in his work, "A New System of Chemical Philosophy." In the same year Gay-Lussac generalized the results of his experiments into the statement of another important law: *When gases combine they do so in simple ratios by volume, and the volume of the gaseous product bears a simple ratio to the volumes of the reacting gases when measured under like conditions of temperature and pressure.*

Dalton did not understand the applicability of Gay-Lussac's discoveries to his atomic theory and so questioned their correctness. The Swedish chemist Berzelius was the first to see the importance of the volume law, and by making the hypothesis that equal volumes of gases under like conditions of temperature and pressure contain equal numbers of *atoms* he made considerable progress in systematizing the chemical data.

But there was one great stumbling block which Berzelius could not pass. Experiment showed that *two* volumes of hydrochloric acid were formed from the combination of *one* volume of hydrogen and *one* volume of chlorine. On Berzelius' view this would mean that *two "atoms"* of hydrochloric acid result from the combination of *one* atom of hydrogen with *one* of chlorine. In other words, the indivisible atoms must have been divided by the reaction.

Although his views were not widely known or accepted until many years later, the way out of this difficulty was made plain by the Italian physicist Avogadro, in 1811. He achieved this simply by introducing the distinction between the *atoms* and the *molecules* of a substance. The molecule of a compound like hydrochloric acid was regarded from the first as being made up of the atoms of the elements of the substances from which it was formed. It was then a natural step to suppose that the units of structure in an elementary (*i.e.*, one which is not a compound) gas were also molecules containing two or more atoms of the elements. This view, due to Avogadro, explains at once Berzelius' difficulty. Thus, if it is supposed that the molecules of hydrogen

and chlorine each contain two atoms, the volume relations come out just right.

The hypothesis of Avogadro may, then, be stated as follows: *Under the same conditions of temperature and pressure, equal volumes of different gases contain the same number of molecules.*

From the experimental point of view the hypothesis is now an established fact. The experimental results in support of it may be briefly enumerated as follows:

1. The complete coordination of the structural formulae of thousands of chemical compounds.

2. Correspondence between positive-ray and mass-spectrograph measurements of atomic weights with those obtained from vapor-density measurements.[1]

3. Results as to the masses of hydrogen and oxygen atoms obtained by Blackett at Cambridge from the study of forked α-particle trails.[2]

4. Concordant values obtained for the number of molecules in a gram-molecule from widely different experimental methods, such as those of Brownian movements and measurement of the charge on an electron.[3]

9. Equipartition of Energy.—The experimental verification of Avogadro's hypothesis, together with the simple kinetic picture presented in the foregoing, now point to an extremely interesting conclusion. This is that the mean kinetic energy of the molecules of all gases is the same at equal temperatures.

Consider a mol of gas A and a mol of gas B in separate containers at the same temperature. Then since the value of R is the same for all gases,

$$RT = P_A V_A = P_B V_B.$$

By Sec. 5 this leads to

$$\frac{1}{3} N_A M_A u_A^2 = \frac{1}{3} N_B M_B u_B^2.$$

Since by Avogadro's rule $N_A = N_B$ it follows that

$$\frac{1}{2} M_A u_A^2 = \frac{1}{2} M_B u_B^2.$$

Had the gases been ideal and were they in the same volume at the same time, the conditions would have been unaltered and the equations deduced above would be applicable. Hence the conclusion *that the mean kinetic energy of the molecules in the two*

gases is the same. This conclusion is a statement, in a limited form, of the principle of equipartition of energy—one of the most important principles of the kinetic theory of gases, concerning which more will be said later.

It is to be noticed that in arriving at the equipartition of energy use was made of the *experimental fact* of Avogadro's rule and the *theoretical equation* relating the product pv to the mean kinetic energy of the molecules. If the kinetic theory is to be fully developed as a set of logical deductions from the assumptions given in Sec. 3 it is evidently necessary that all conclusions be obtained on an entirely theoretical basis. From the discussion just given it is seen that if Avogadro's rule were derived theoretically, assuming equipartition, then the theory would be in perfect and independent accord with experiment. The theoretical deduction of the rule is one of the important mathematical triumphs of the kinetic theory which will be discussed in detail later. The theory as usually presented proceeds, it will be interesting to observe, in the opposite order from that pointed out by experimental developments, in that the equipartition of energy is given theoretical discussion, and from this Avogadro's rule is derived instead of conversely.

10. The Law of Partial Pressures.—John Dalton, pioneer student of atomic theory, discovered the experimental law governing the pressure exerted by a mixture of several gases which do not react chemically. The results of his investigations in this field may be stated as follows: *The total pressure exerted by the mixture is equal to the sum of the pressures which the several gases would separately exert if each were to occupy the vessel alone.*

In developing the kinetic-theory view of this law it is to be supposed that the molecules of different kinds exert no forces on each other, other than the elastic forces introduced by collisions. Then on making a mixture of gases no kinetic energy will be gained or lost provided the impacts are perfectly elastic as previously assumed, so that the total kinetic energy will be equal to the sum of the kinetic energies of the gases put into the mixture.

In accordance with the simple theory given, the total pressure exerted by the mixture P will be related to the total kinetic energy E by the equation

$$P = \frac{2}{3}\frac{E}{v},$$

where v is the volume. On the other hand, the partial pressures or pressures which each gas would exert if it alone filled the space are given by equations of the same form

$$P_1 = \frac{2}{3}\frac{E_1}{v}; \quad P_2 = \frac{2}{3}\frac{E_2}{v}; \quad P_3 = \frac{2}{3}\frac{E_3}{v}; \text{ etc.,}$$

so that, since

$$E = E_1 + E_2 + E_3 + \ldots,$$

it follows that

$$P = P_1 + P_2 + P_3 + \ldots,$$

which is nothing other than Dalton's law of partial pressures.

11. Molecular Speeds.—The results which have been obtained already allow the calculation of the mean speed of the molecules. From Sec. 6

$$pv = \frac{1}{3}\nu m u^2.$$

Now νm is the total mass of the gas, so on dividing by v and writing ρ for the density of the gas the result is:

$$p = \frac{1}{3}\rho u^2$$

$$u = \sqrt{\frac{3p}{\rho}}.$$

The density and the pressure of a gas are quantities which are known experimentally and so u may be computed. Thus at 1 atmosphere pressure and at 0°C. the density of nitrogen is 0.00125 gram per cm^3. Atmospheric pressure is $76 \times 13.6 \times 980$ dynes per cm^2, so substitution in the formula yields

$$u = 4.93 \times 10^4 \text{ cm per sec.}$$

Another way of arriving at this result shows the relation between the molecular speed, the molecular weight, and the temperature. Combining the empirical equation of state with the theoretical equation,

$$RT = \frac{1}{3}N_A m u^2$$

$$u^2 = \frac{3RT}{N_A m} = \frac{3RT}{M},$$

where M is the molecular weight of the gas in grams, R applies to a mol, and N_A is the number of molecules in a mol.

In the deductions of this chapter, it may again be emphasized that all of the molecules were regarded as having the same speed. It will be seen later (Sec. 27) that this is not actually the

case, and that when a gas is held at constant temperature and pressure the molecular speeds are distributed about their mean value in such a way that most of them are very close to the mean, but a few are very small and a few are very great. The speed which has just been calculated for the molecules is the speed which each of the molecules must have in order that the total kinetic energy be the same as that actually possessed by the gas.

Such a speed is a kind of mean speed which is different from the ordinary arithmetic mean of the actual speeds of the individual molecules. Let v_1, v_2, v_3, . . . v_ν be the actual speeds of each molecule at any instant, then the arithmetic mean of the speeds would be simply

$$v = \frac{1}{\nu}(v_1 + v_2 + v_3 + \ . \ . \ . \ + v_\nu).$$

On the other hand, if u is the single speed which makes the total kinetic energy the same as the actual kinetic energy,

$$\frac{1}{2}\nu m u^2 = \frac{1}{2}m(v_1^2 + v_2^2 + v_3^2 + \ . \ . \ . \ + v_\nu^2)$$

or

$$u^2 = \frac{1}{\nu}(v_1^2 + v_2^2 + v_3^2 + \ . \ . \ . \ + v_\nu^2).$$

From this it is evident that u is the square root of the arithmetic mean of the squares of the velocities. It will hereafter be referred to simply as the root-mean-square speed. As the square root of the average squares in averaging emphasizes the larger numbers, such an average is always greater than the arithmetic average. Thus the theoretically inferred root-mean-square average velocity calculated for the real molecules having a distribution of velocity values will be slightly greater than the arithmetic average usually used.

The average molecular velocities which for a gas like N_2 are of the order of 10^4 to 10^5 cm/sec., as was seen, are great compared to the velocities encountered in everyday experience. An automobile making 60 miles an hour has a speed of 2.68×10^3 cm/sec. An ordinary 22-caliber rifle bullet has a speed less than, but near that of, the molecules, while the modern army rifle bullet has a speed of the order of 8.24×10^4 cm/sec. The speed of a projectile fired directly away from the earth, which will enable the projectile to escape from the earth against gravi-

tational attraction (the so-called velocity of escape) is 1.1×10^6 cm/sec., while on the moon the velocity of escape is 2.4×10^5 cm/sec. Perhaps the best speed with which to compare that of the molecules is that of sound waves in the same gas. In elementary treatises on sound waves it is shown that this velocity v depends on the pressure and density in the following way:

$$v = \sqrt{\frac{\gamma p}{\rho}},$$

in which γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume. For perfect monatomic gases it will be seen later that it is a consequence of the kinetic theory, also borne out by experience, that $\gamma = 5/3$, so that

$$\frac{v}{u} = \sqrt{\frac{\gamma}{3}} = \frac{1}{3}\sqrt{5} = 0.7452,$$

which leads to the interesting conclusion that the velocity of sound in a perfect monatomic gas is approximately three-fourths of the mean speed of the molecules in that gas. This fact is not surprising in that sound waves are carried by molecular motions.

The expression (deduced on page 26) $u^2 = 3RT/M$ or $u = \sqrt{3RT/M}$ indicates that u is proportional to the square root of T, the absolute temperature, and inversely proportional to the square root of M, the molecular weight of the molecule. As this expression does not contain pressure or density, it is seen that the velocity u is independent of these quantities. The reason lies in the fact that while $u = \sqrt{3p/\rho}$, p and ρ are so related that a variation in one implies a like variation in the other. Finally, it is of interest to calculate the average kinetic energy of a gas molecule at some standard temperature. Since $RT = pv = \frac{1}{3}N_A m u^2$, it follows that the kinetic energy $KE = \frac{1}{2}mu^2 = \frac{3}{2}\frac{RT}{N_A}$. Here R is the gas constant per mole, and N_A is the number of molecules in a gram-molecule or mole, *i.e.*, the Avogadro number. If $T = 273°$abs. or 0°C. and $N_A = 6.064 \pm 0.006 \times 10^{23}$, then $\frac{1}{2}mu^2 = KE = 5.617 \times 10^{-14}$ erg. The ratio R/N_A is often written as $R/N_A = k$, where k is called the Boltzmann constant, which has the value $k = 1.3708 \times 10^{-16}$ erg per degree. Accordingly, the expression for the kinetic energy is often written $\frac{1}{2}mu^2 = KE = \frac{3}{2}kT$.

12. Slow Diffusion, the First Paradox of the Kinetic Theory. Since the theory requires such enormous speeds for the molecules, the natural inquiry is, why it is that the molecules are not observed (by their direct effects) to travel so rapidly. Thus, at first sight, it might seem that a little hydrogen released in one corner of a large room should be observed in other parts of the room a fraction of a second later.[4] This seeming contradiction was raised against the kinetic theory in its earliest days as a serious difficulty. The answer lies in the evaluation of the enormous number of the molecules in a cm^3. It is thus obvious that the number of collisions experienced by a molecule in a short time will be enormous. Each collision deflects the molecule from its straightforward course; in fact, it may reverse the direction of its motion; so it is easy to see the answer to the seeming contradiction of theory and experience.

The proper development of an explanation for the slowness of diffusion of gases and other related matters opens up a whole division of kinetic theory—that which deals with the concept of the mean free path of the molecules. Discussion of this will be reserved for the next chapter. Now, however, the results of the further developments may be anticipated by the statement that the average distance between molecular collisions will be found to be about 10^{-5} cm under usual gas pressures.

References

1. THOMSON, J. J.: "Rays of Positive Electricity," Longmans, Green & Co., London, 1921. ASTON, F. W.: "Isotopes," 1st ed., Edward Arnold & Co., London, 1922; 2d ed., 1924.
2. BLACKETT: *Proc. Roy. Soc.*, **A103**, 720, 1923.
3. MILLIKAN, R. A.: "The Electron," pp. 144, 238, University of Chicago Press, Chicago, 1917.
4. CLEMENS-SCHAEFER: "Einführung in die Theoretische Physik," vol. 2, part I, Sec. 85, p. 363, Vereinigung Wissenschaftlichen Verleger, Berlin, 1921.

Books Recommended

a. MEYER, O. E.: "Kinetic Theory of Gases," Chaps. I, II, Longmans, Green & Co., London, 1899.
b. PRESTON: "Theory of Heat," Chap. I, Secs. 6, 7, also Chap. IX, Macmillan & Co., Ltd., London, 1919.
c. EDSER, E.: "Heat for Advanced Students," Macmillan & Co., Ltd., London, 1910.
d. SMITH, ALEXANDER: Avogadro's Hypothesis and the Kinetic Theory, in "General Inorganic Chemistry," Chaps. IX, XII, The Century Co., New York, 1907.

e. CLAUSIUS, R.: "Die Kinetische Theorie der Gase," Chap. I, F. Vieweg und Sohn, Braunschweig, 1889.

f. SAHA and SRIVASTAVA: "A Text Book of Heat," Chap. III, Indian Press, Allahabad, 1931.

g. JAUNCEY, G. E. M.: "Modern Physics," Chap. VII, D. Van Nostrand Company, New York, 1932.

h. HERTZFELD, K. F.: Kinetische Theorie der Wärme, Müller-Pouillet, "Lehrbuch der Physik," 11th ed., vol. 3, part II, Vieweg und Sohn, Braunschweig, 1925.

i. JÆGER, G.: Die Kinetische Theorie der Gase, Geiger und Scheel, "Handbuch der Physik," vol. 9, Chap. VI, Julius Springer, Berlin, 1926.

j. CASTELFRANCHI, G.: "Recent Advances in Atomic Physics," W. S. Stiles and J. W. T. Walsh, vol. 1, Chap. III, J. and A. Churchill, London, 1932.

CHAPTER III

THE MEAN FREE PATH—CLAUSIUS' DEDUCTIONS

13. Concept of Free Path.—Continuing the development of the mechanical model of a gas, begun in the last chapter, it is now of importance to consider the question, How far do the molecules travel, on the average, between their successive collisions with each other and with the wall? At the end of Chap. II it was foreshadowed that the answer to this question would make clear the slowness of gaseous diffusion in the face of the great molecular speeds.[10] It will also be seen that the heat conductivity and the viscosity of gases are intimately tied up with the question of the mean free path.

In the preceding developments, the molecules of a gas have been regarded as perfectly elastic spheres whose diameters were vanishingly small compared to the mean distance apart of the molecules. The gas molecules were thought of as moving with a velocity u such that the total kinetic energy of the translatory motion was the same as the total kinetic energy of the actual translatory motions (Sec. 11). As the molecules exert no forces on each other except during collision, their paths between collisions will be rectilinear and described at constant speed. At certain times in the life history of a molecule it may happen that the molecule will go a comparatively great distance between successive collisions, at others two successive collisions will come very close together. In other words, the distances traveled between successive collisions, *i.e.*, the free paths, will be widely different, but will be distributed around a certain mean value. This mean distance traveled by a molecule between successive collisions is defined as the mean free path.

Kinetic theory owes this very fruitful concept to Clausius,[9] who opened up a whole new branch of investigation by its introduction. He was led to these considerations by the very difficulty which has already been noted—that of the slow diffusion of gases.

Let n be the average number of collisions experienced by a molecule in a second, then $1/n$ is the average time between collisions, and if the mean speed be u cm/sec., the mean free path L in cm will be given by

$$L = \frac{u}{n}.$$

The evaluation of the mean free path is thereby made to depend upon the calculation of the average number of collisions which a molecule experiences in a second. This is the mode of approach to the problem originally adopted by Clausius. The deduction of this number, following the argument of Clausius, will now be given.

14. Number of Collisions.—Let the diameter* of the molecules be denoted by σ and consider a gas comprised of ν molecules occupying a container of volume V and of surface Σ. Actuated by their thermal motions, the molecules will be moving about in a random manner, as often in one direction as in another, with the mean speed u. For simplicity, the molecules will all be supposed to have the same speed, as in preceding arguments.

When a molecule collides with the wall its center comes to a distance of $\frac{1}{2}\sigma$ from the wall. When a molecule collides with another molecule the minimum distance between the centers of the two molecules will be σ. If, then, the attention be fixed on one particular molecule, it is seen that there are certain regions of the containing vessel which cannot be occupied by the center of this particular molecule. For convenience, call the center of this molecule A. Then A certainly cannot be within a distance of $\frac{1}{2}\sigma$ from the wall, nor can it lie within any sphere described about the center of any of the molecules with a radius equal to the diameter of the molecules.

It is thus seen that the collisions experienced by the molecule A may be discussed by considering the collisions of the point A its center, with the surface S, which bounds the regions in which A can lie. In other words, the question of the collisions of spherical molecules with other such molecules or with the walls may

* For the discussion of the meaning of σ the student is referred to Sec. 19 and Secs. 49 and 52 in Chap. V.

be replaced by the equivalent problem of the collisions of a point with a surface.

The surface S may be better visualized by considering how an instantaneous picture of the molecules would look. It would find each molecule situated at a certain point within the volume V (Fig. 2). Surrounding each molecule would be a sphere of radius σ, these spheres constituting part of the discontinuous surface of exclusion S, the remaining part of S being a surface parallel to the walls of the vessel but distant $\frac{1}{2}\sigma$ from them. The point A might, then, with equal likelihood, occupy one part of the space within this surface as another. The volume available to A will be denoted by U.

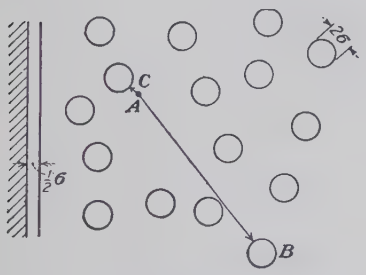

FIG. 2.

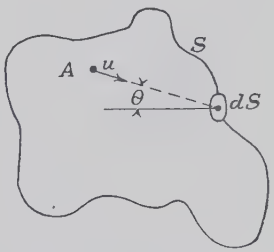

FIG. 3.

But all of the equally likely positions of A are not associated with equal probability of collision with the surface S. Consider an element dS of the surface S toward which the molecule is moving in such a direction that its path makes an angle θ with the normal to dS (Fig. 3). The chance that the molecule will strike dS in the time dt depends on the relative motion of the molecule and this portion of S. Regarding the molecule as stationary, the element dS will move toward A with a speed u sweeping out a volume

$$u \cdot dt \cdot dS \cdot \cos \theta.$$

If at the time t the point A is anywhere within this volume, it will collide with dS during the time t and $t + dt$. As all positions of the molecule are equally likely, the probability P_{dtdS} of a collision with dS in time dt may be written:

$$P_{\theta . dtdS} = \frac{u \cdot \cos \theta}{U} \cdot dt \cdot dS.$$

This expression depends on the angle of approach of A toward dS. This element may be eliminated by averaging over all of the equally probable directions of approach. Take the normal to dS as the axis of polar coordinates. The probability P of A approaching dS in a direction contained between θ and $\theta + d\theta$ will be proportional to the solid angle at dS subtended by these directions. This element of solid angle is measured by the area on a sphere (Fig. 4) of unit radius of the circular zone between the angle θ and $\theta + d\theta$ and so is equal to

$$2\pi \cdot \sin\theta \cdot d\theta.$$

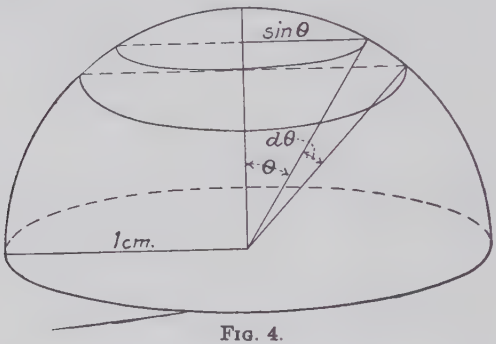

FIG. 4.

The total solid angle about a point is 4π, so the chance that θ lies between θ and $\theta + d\theta$ is

$$\frac{2\pi \sin\theta d\theta}{4\pi} = \frac{\sin\theta d\theta}{2}.$$

But it is evident that a collision of A with dS is possible only when $\theta < \frac{\pi}{2}$, so that the chance of collision of A with dS in time dt, in a form independent of θ, is

$$P_{dtds} = \frac{u}{2U}\int_0^{\frac{\pi}{2}} \cos\theta \sin\theta \cdot d\theta dt ds = \frac{u}{4U} \cdot dt \cdot dS.$$

As this chance is independent of the particular part of S under consideration, it may be integrated at once over the whole surface:

$$P_{Sdt} = \frac{uS}{4U} \cdot dt.$$

The expression on the right is then the probability that A will collide with any part of the surface S in the time dt. The greater this time interval, the greater is the likelihood of a collision. As

the probability does not depend on the particular instant chosen, dt may be replaced by a finite time interval Δt. Choose Δt so that the probability $P_{s\Delta t}$ is equal to unity, *i.e.*, certainty of a single collision. The proper value of Δt is, evidently,

$$\Delta t = \frac{4U}{uS}.$$

Supposing that the amount of time consumed in a collision is negligible, the number of collisions in unit time is then

$$n_1 = \frac{1}{\Delta t} = \frac{uS}{4U}.$$

15. The Quantities S and U.—In the expression just found for the number of collisions in unit time, the quantity S is the total area of the surface on which A, the center of a particular molecule, might collide. It is made up of two parts: (1) the total area of the spheres drawn about all the other molecules with a radius equal to the diameter of the molecules, and (2) the total area of a surface which is generated as the locus of a point which is at all times distant $\frac{1}{2}\sigma$ from the walls of the containing vessel. The first term is simply equal to $4\pi(\nu - 1)\sigma^2$, and since in all cases ν, the number of molecules in V, is enormously great compared to unity, this may be taken as $4\pi\nu\sigma^2$. The second term is quite negligible in comparison with the first in most cases, so that in all cases the much smaller difference between it and Σ, the total area of the walls of the containing vessel, may be ignored. This fact can readily be seen from the following calculation: The surface area of a sphere of radius 1 cm is 4π cm^2. The volume is $\frac{4}{3}\pi$ cm^3. This contains, at N.T.P., 11.3×10^{19} molecules each of radius about 1×10^{-8} cm, and of radii of spheres of exclusion of 2×10^{-8} cm. The surface of each sphere is $16\pi \times 10^{-16}$. The total area of the spheres in this volume is $\frac{4}{3}16\pi^2 \times 2.7 \times 10^3$ cm^2, or 5.7×10^5 cm^2. This is 4.5×10^4 times as great as the surface of the spherical vessel with the molecules in it.

The quantity U, it will be remembered, is the total volume available to the point A. It is evidently somewhat less than the total volume of the containing vessel V. Let the difference be denoted by b, so that

$$U = V - b.$$

This difference b may, like S, be naturally regarded as the sum of two parts: (1) the volume from which A is excluded by virtue of the presence of the other molecules, and (2) the volume of the region within $\frac{1}{2}\sigma$ of the walls of the container. Further consideration of the value of b will be undertaken later (Sec. 19).

16. Approximate Free Path.—Introducing the expressions for U and S in the formula for the mean number of collisions per second of a given molecule,

$$n_1 = \frac{u \cdot (\Sigma + 4\pi\nu\sigma^2)}{4(V - b)}.$$

The relation $L = u/n_1$ between number of collisions and free path then gives the free-path formula:

$$L = \frac{4(V - b)}{\Sigma + 4\pi\nu\sigma^2}.$$

In many cases, the quantity b is negligibly small in comparison with V, and Σ is also negligible in comparison with $4\pi\nu\sigma^2$ (see end Sec. 15). By Sec. 19, b is $\frac{2}{3}\pi\sigma^3 N$. That is, b for molecules of $\sigma = 2 \times 10^{-8}$ cm for a cm^3 of gas at N.T.P. is $\frac{16}{3}\pi \times 10^{-24} \times 2.71 \times 10^{19}$ cm^3, or 4.5×10^{-4} cm^3, while V is 1 cm^3. Another way of getting at this is by considering the volume of a given mass of water compared to that occupied by the same mass of steam or water vapor. Eighteen grams of water occupy, roughly, 18 cm^3. In the gaseous state 18 grams of water would occupy 22,410 cm^3 of volume. Moreover, in the aqueous state the volume occupied by the water molecules is still greater than b. Dropping Σ and b from the expression, the free-path formula simplifies into:

$$L = \frac{V}{\pi\nu\sigma^2}.$$

Denoting by $N = \nu/V$, the number of molecules per cm^3 of the gas, *i.e.*, the molecular density, the formula may be written

$$L = \frac{1}{\pi N\sigma^2}.$$

It is obvious from this expression that the mean distance between molecular impacts is dependent only on the molecular diameter σ and the number of molecules per cm^3. This formula makes it evident that *the mean free path is inversely proportional to the molecular density.* Since for equal volumes and temperatures the

pressure exerted by a perfect gas is known to be proportional to the molecular density, the important result follows that *the mean free path is inversely proportional to the pressure.*

Elementary Deduction.—A simple deduction of the expression for the mean free path may be made as follows: Assume all the other molecules at rest and one molecule moving with a velocity u. If the center of any other molecule comes within σ cm from the first they will collide (Fig. 5). Thus, as the moving molecule moves u cm in 1 sec., there will be a volume $\pi\sigma^2 u$ which contains all the molecules with which it collided. If there were N molecules per cm^3 in the volume, that means that the moving molecule in going u cm in the gas in 1 sec. collided with $\pi N\sigma^2 u$ molecules. The average distance gone between collisions L is, therefore, u, the distance traversed, divided by $\pi N\sigma^2 u$, the number of impacts experienced. Thus $L = u/(\pi\sigma^2 Nu)$ or $L = 1/(\pi\sigma^2 N)$.

This is the same formula as the simplified expression above.

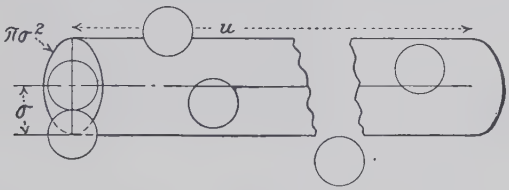

FIG. 5.

17. Relative-velocity Correction.—In Sec. 14, when the mean number of collisions per second experienced by a particular molecule was being evaluated, one assumption was tacitly made, correction for which will now be developed. In computing the probability of collision of a point A with an element of the surface S, the speed of approach of the point A to the element dS was taken simply as the root-mean-square speed of the molecules.

Actually, the quantity which should be used is the mean *relative speed* of the point A and the surface S. Now part of the surface S is that which is parallel to the walls of the vessel. The mean relative speed of the point A with respect to the walls is simply the root-mean-square speed of the molecules as used. The principal part of S, however, consists in the spheres of radius σ which surround all of the other molecules. In the preceding derivation, when these were regarded as at rest, the relative speed of A and of this part of S was correctly taken as u. It is now necessary to examine the effect of making a hypothesis more in accord with

the facts—that the other molecules are also moving in all directions with the same* *mean speed* equal to u.

This requires that the mean relative speed of two molecules which each move with the same speed, but for which all directions of motion are equally probable, be calculated. The relative speed of two molecules is the vector difference of their speeds when these are referred to the same reference system (Fig. 6). If θ is the angle between the directions of motion, the magnitude of this vector difference ξ is evidently given by

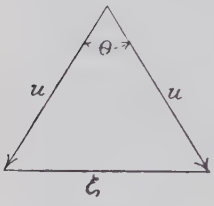

Fig. 6.

$$\xi = 2u \cdot \sin \frac{1}{2}\theta,$$

since ξ is the base of an isosceles triangle, whose two equal sides are each equal to u, and in which the angle opposite ξ is θ. ξ is to be averaged over all values of θ, taking account of the equal weighting of the solid angle in the various directions around the vertex of θ. This is accomplished as before (Sec. 14) by multiplying ξ by $2\pi \cdot \sin\theta \cdot d\theta$. Integrating from 0 to π, and dividing by 4π, the mean value $\bar{\xi}$ is then

$$\bar{\xi} = \frac{1}{4\pi}\int_0^\pi 2u \sin\frac{1}{2}\theta \cdot 2\pi \sin\theta d\theta = 2u\int_0^\pi \sin^2\frac{\theta}{2}\cos\frac{\theta}{2}\,d\theta$$
$$= \frac{4u}{3},$$

or the mean speed of the molecules relative to each other is four-thirds their root-mean-square speed when all the molecules are treated as moving with the same speed.

Returning to the equation of Sec.(16) for the mean number of collisions per second, it is seen that this can better be written:

$$n_1 = \frac{u\Sigma}{4(V-b)} + \frac{\frac{4}{3}\pi\nu\sigma^2 u}{V-b},$$

the first term representing collisions with the walls and the second collisions of the molecules with each other introducing the relative-velocity correction. Supposing as before that Σ is negligible in comparison with the area of the spheres of exclusion, a new expression is obtained for the free path as follows:

* This assumption of equal molecular speeds introduces an error which will later need modification (see Sec. 37, Chap. IV).

$$L = \frac{V - b}{\frac{4}{3}\pi\nu\sigma^2}.$$

Again making the lesser approximation in neglecting b, the expression for the mean free path appears in the form

$$L = \frac{V}{\frac{4}{3}\pi\nu\sigma^2} = \frac{1}{\frac{4}{3}\pi N\sigma^2}.$$

Dividing both sides of the equation by σ, this yields

$$\frac{L}{\sigma} = \frac{1}{\frac{4}{3}\pi N\sigma^3},$$

so that the mean free path bears the same ratio to the diameter of the molecules as does the total volume of the vessel to the total volume of the spheres of exclusion, or as does the total volume to eight times the volume of the molecules.

The free-path expressions which have been obtained by correcting for the mean relative speed are the same as given originally by Clausius in 1858. In their derivation it is to be noticed that the molecules are regarded as all having the same speed u, all directions of motion being regarded, however, as equally probable.

18. Clausius' Pressure-volume Relation.—In Chap. II, the deduction of the equation embracing the experimental results of Boyle and Charles was based on the original method of Joule, who found it necessary to regard the molecules as all having the same speeds, and certain fractions of them moving perpendicularly to each of the walls of the containing box. By arguments similar to those used in arriving at the mean free path, Clausius was better able to face the facts by supposing all directions of motion equally probable in giving a theoretical deduction of this equation. He was, however, still bound to the assumption that all the molecules travel with the same speed. The number of collisions per second which each molecule makes with S, in which the molecule strikes at an angle between θ and $\theta + d\theta$ with the normal to S, was found by Sec. 14 to be

$$\frac{Su \sin\theta \cos\theta d\theta}{2U}.$$

If ν molecules are contained in the available volume, $V - b$, the number of collisions is

$$N_{s\theta} = \frac{S\nu u \sin\theta\cos\theta d\theta}{2(V-b)}.$$

From the dynamics of perfectly elastic collisions between smooth bodies, it is known that when a smooth elastic sphere collides with an elastic plane the normal component of the momentum of the ball is reversed while the tangential component is unaffected. In having the normal component of its momentum reversed, the ball communicates to the wall an impulse equal to the total change of momentum which is evidently twice the normal component. If the velocity of the molecule of mass m relative to the wall is u, the normal component of the velocity is $u \cdot \cos\theta$, so that the impulse communicated to the wall at each collision is

$$2mu\cos\theta.$$

The impulse communicated per second, *i.e.*, the force exerted by all the molecules which collide at an angle between θ and $\theta + d\theta$, is

$$f_\theta = \frac{2\nu S u^2 m\cos^2\theta\sin\theta d\theta}{2(V-b)}.$$

As collisions occur only when $\theta < \pi/2$, the force exerted on the surface by all the collisions will be obtained on integrating this expression with respect to θ from 0 to $\pi/2$.

$$\int_0^{\frac{\pi}{2}} f_\theta d\theta = \frac{\nu S u^2 m}{V-b}\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta = \frac{\nu S u^2 m}{V-b}\left[-\frac{\cos^3\theta}{3}\right]_0^{\frac{\pi}{2}} = \frac{\frac{1}{3}\nu m u^2 S}{V-b}.$$

The pressure exerted by the gas on the walls is the force per unit area, so that the last expression leads to the following expression for the relation between the pressure and volume of a gas:

$$p(V-b) = \frac{1}{3}\nu m u^2.$$

This is the thoeretical equation as developed by Clausius.

Comparing the Clausius equation with that of Joule (Sec. 5), it is seen that the two correspond exactly except that the Clausius equation makes provision for the term b, representing the influence of the finite size of the molecules. Following upon the pioneer work of Boyle, experimenters found that there were small deviations from the inverse proportionality of pressure and volume. These slight deviations have their origin in two things:

(1) the finite size of the molecules, and (2) cohesive forces acting between the molecules in addition to those which come into play during collisions. The Clausius equation shows how the first should affect the pressure-volume relation. The way in which the second acts will, of course, depend on the nature of the supposed intermolecular forces. This point will be given detailed discussion later (Sec. 48, Chap. V).

19. The Quantity b.—This quantity, which occurs in the free-path expressions as well as the pressure-volume equation of the gas, was first introduced in Sec. 15 simply as the difference between the actual volume of the vessel and the somewhat smaller volume which is available for the motion of the point A. It was there seen to be made up of a thin layer along the walls of the vessel and a part which depends in some way upon the volume of the molecules themselves.

It is now desirable to take up the study of the way in which b depends on the volume of the molecules. This amounts to a complete determination of b for all practical purposes, since the contribution of the layer along the walls is negligible. At first sight, it might be supposed that b for the gas in 1cm^3 at N.T.P. is simply equal to the total volume of the spheres of exclusion. Since these are spheres of radius equal to the diameter σ of the molecules, this would give

$$b = \frac{4}{3}\pi N\sigma^3,$$

where N is the number of molecules per cm^3.

Actually, however, b is only one-half of the value given. This may be seen to be the case by considering the collisions of a single molecule of radius equal to that of the sphere of exclusion, *i.e.*, equal to the diameter of the molecules, with the points which represent the centers of the other molecules. In a collision of such a sphere with a point only that half of the sphere which is directed toward the line of relative motion of sphere and point is active in excluding the point from a volume. This is exactly true for binary encounters between molecules. It is conceivable that there is occasionally a collision in which three or even more molecules are involved at once, but it may be shown that such cases are extremely rare. The correction due to ternary and higher collisions is quite unimportant in comparison with the approximation already made in assuming spherical molecules.

The value of b is then to be taken as

$$b = \frac{2}{3}\pi N\sigma^3.$$

As will later be seen, b can be experimentally determined, and hence if N is known, σ may be evaluated. The deduction makes it possible, however, to use this relation only down to gas volumes of $\frac{4}{3}\pi N\sigma^3$ or $2b$, since for volumes less than this the equal probability of all kinds of impacts is altered by the limitations of the space available. According to Van der Waals, such a change in the value of b actually occurs for gas volumes less than $2b$, as will be seen in Sec. 52.

20. Number of Molecules Striking Unit Surface per Second.— It is often of interest to determine the number of molecules striking a surface per second. The knowledge of this quantity is very useful in calculations of heat transfer to solid surfaces and for problems of evaporation when equilibrium exists. In this section two short deductions will be given. In the next chapter a more rigorous deduction will also be given involving the distribution of the free paths and the velocities among the molecules.

In Sec. 14 it was found that the chance P_s of a single molecule striking a surface S per second was $P_s = Su/4U$, where u is the average velocity and U the volume of the vessel.* If there are n molecules in U the number striking S per second is given by $P_s n = N_s$. Thus $N_s = nSu/4U$, and calling $n/U = N$ the number of molecules per cm^3, $N_s = SNu/4$. If $N_s/S = N_1$, the number striking a cm^2 per second, then

$$N_1 = \frac{Nu}{4}.$$

Again it is possible to proceed as follows. Assume a cm^2 of surface with N molecules per cm^3 in the space above it. Of these molecules the chance that one has a velocity so directed as to make an angle θ with the normal to the surface is $\sin \theta d\theta/2$ (see Sec. 14). Of the N molecules in a cm^3 only those which lie in a parallelepiped u cm long and of base $1 \times \cos\theta$ cm^2 will strike the surface in 1 second, for those farther away will not reach it in 1 second going u cm/sec.; and only those that lie in the cylinder whose base has the area normal to the direction of motion $1 \times \cos\theta$ cm^2 can strike it at an angle θ with the normal. Thus if there are N molecules per cm^3, only those in the volume $u \cos\theta$, to wit, Nu

* Note that here the volume U is used interchangeably with V which is permissible as b is very small.

cos θ, will be in a position to strike the surface, and of these the chance of striking the surface at θ is sin $\theta d\theta/2$. Hence the number striking at an angle θ is given by

$$N_\theta = u \cos \theta \frac{N}{2} \sin \theta d\theta.$$

Integrating θ from 0 to $\pi/2$ to cover all space above the surface, the result is

$$N_1 = \frac{Nu}{2} \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta = \frac{Nu}{4}.$$

21. The Distribution of Free Paths.—The conception of the average, or mean, free path recently deduced gave the *average value* of the distance which a molecule had to move between two successive impacts. It was assumed in the process of averaging that the motion of the molecule in any direction was equally probable, and that the molecule might be at any point in the volume. That is, it was assumed that enough points and directions were taken in averaging in order to permit this to hold true. Actually, in looking at one of the instantaneous pictures of the surfaces of exclusion surrounding the point molecule A (Sec. 14), the molecule is pictured surrounded by a very irregular surface. If, then, from any point A where it happened to be this molecule were to move in a direction AC (Fig. 2) it would strike the wall after having traversed a very short stretch. If, however—what is equally probable—the point molecule should move in the direction AB, the distance moved before impact would be quite long. Thus, while a mean value for the free path is spoken of, the paths actually traveled are not equal, but may take on any value. The fact that these paths depend on pure chance for their single values will make it possible to derive an expression giving the distribution of the paths among the molecules.

The law of distribution of free paths may be derived as follows: Consider I molecules starting out from a collision. After these have gone a distance x the number which has not yet experienced a collision is denoted by y. If a molecule, on the average, has Z collisions per second and its speed is u, the probable number of collisions in 1 cm is Z/u and the probable number of collisions in going a distance dx is $(Z/u)\,dx$. This is, however, equal to the decrease in y, *i.e.*, to $-dy$, for y decreases as x increases. Therefore, it is possible to write $dy = -\frac{Z}{u} y dx$.

Separating the variables, $dy/y = -(Z/u)\,dx$, and integrating between the limits $y = I$ at $x = 0$, and $y = y$ at $x = x$, the result is $\log y - \log I = -Zx/u$,

or $$y = Ie^{-\frac{Z}{u}x}$$

and $$dy = -\frac{Z}{u} Ie^{-\frac{Z}{u}x}\,dx.$$

It is important to note in this place that in deducing this equation the tacit assumption was made in writing $-dy = \frac{Z}{u}y\,dx$ that the chance of a collision depended on $\frac{Z}{u}y$ and dx only. That is, the number of impacts dy was governed by the distance traversed dx, by the number of molecules traversing it, and by a constant factor which gives the probable number of molecules experiencing a collision in 1 cm. This constant is what might be called a "scale factor" and is the constant of proportionality which determines the absolute value of the path. The derivation therefore assumes the independence of the free path executed from all other factors than y, dx, and Z/u.

To obtain a meaning for the constant Z/u it merely becomes necessary to determine the average free path, or mean free path L. This is obtained by multiplying the number of molecules dy of path between x and $x + dx$ by x, the length of the path, summing it for all the groups of molecules from 0 to I, and dividing by I. Thus the mean free path,

$$L = \int_0^I \frac{x\,dy}{I} = \int_\infty^0 \frac{-I\frac{Z}{u}e^{-\frac{Z}{u}x}}{I}\,x\,dx.$$

$$L = -\frac{Z}{u}\left[-\frac{xe^{-\frac{Z}{u}x}}{Z/u}\right]_\infty^0 + \frac{Z}{u}\int_\infty^0 \frac{-e^{-\frac{Z}{u}x}}{Z/u}\,dx = \frac{u}{Z}.$$

Hence $L = u/Z$ and the equations above become

$$y = Ie^{-\frac{x}{L}}.$$

$$dy = -\frac{I}{L}e^{-\frac{x}{L}}\,dx.$$

Thus out of I paths that start anew after their last collision $Ie^{-\frac{x}{L}}$ have a path exceeding x cm in length. The larger the value of L, the average path, the more paths there will be that exceed a given

x. The number dy out of the I paths that end in a specific fractional interval dx/L of the mean free path (*i.e.*, in a certain interval between x and $x + dx$ whose length is a fraction dx/L of the mean path L) is $Ie^{-\frac{x}{L}}dx/L$. Thus by choosing an adequate interval dx/L the number of impacts suffered in that interval can be found. It may be seen from the equation that both the curves for y and dy as a function of x are exponential curves. At the point $x/L = 0$, $y = I$, and at increasingly large values of

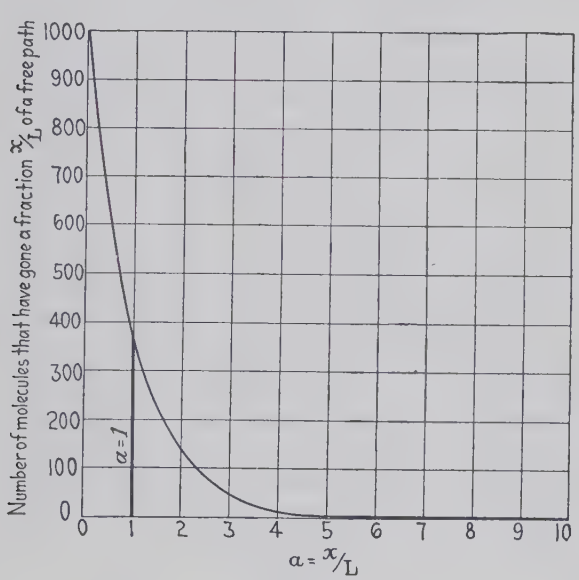

FIG. 7.

x/L, y approaches 0 asymptotically. The curve for y as a function of x/L is given in Fig. 7. Thus it can be seen from Fig. 7 that out of 1000 molecules starting at $x = 0$, 670 go a distance $x/L = 0.40$, 370 go a distance $x/L = 1$, and 18 go a distance $x/L = 4.02$. The point marked in the Fig. 7 by the vertical line is the point at which $x/L = 1$. It is the point where x equals the mean free path and it is the center of gravity of the distribution curve. It is to be noted that in this distribution curve the free paths have all values and are not grouped closely on either side of the mean value as will be found to be the case for the distribution of velocities (Sec. 35, Chap. IV).

22. The Mobility of Gaseous Ions (an illustrative application of the free-path distribution).—As an example of the use of the concept of the free paths and of the importance of taking into account the distribution of the free paths, the evaluation of the velocity of gaseous ions deduced on the kinetic theory may be used. The normal gas ion, the carrier of electricity in gases, could be assumed to consist of a single molecule* carrying an extra positive or negative charge (see Sec. 102 of Chap. XI).

If such a charged molecule be placed in a field of strength X volts per cm in a gas it would experience the acceleration Xe/m due to the action of the field, where e is its charge and m its mass. The acceleration cannot last for a long time, however, as the ion soon collides with a neutral molecule of its own mass. If a large number of such impacts be regarded, it may be assumed (see Sec. 103) that at each impact the velocity gained by the ion in the direction of the field is annihilated. It must then begin its acceleration in the field anew after each impact. If the ion makes many millions of collisions in going a centimeter in the direction of the field this will result in the ions having a uniform average velocity of drift in the direction of the field. This velocity reduced to unit field strength is called the "mobility" of the ion. This reduction assumes velocity proportional to field strength, a fact borne out by experiment. It is thus obvious that the mobility must largely depend on the acceleration over a mean free path, and that hence the mean free path must be an important feature in the evaluation of the mobility. In deducing the expression for mobilities as here given the following assumptions must be made:

1. Ions do not exert forces on the neutral molecules, *i.e.*, the paths are not influenced by the ionic charge.

2. The impacts between ions and molecules as between molecules and molecules are perfectly elastic.

3. The mass of the molecule equals that of the ion.

4. The field is so weak that the gain in energy of the ion from the field over a single free path is small compared to the energy of agitation of the gas molecules.

* The nature of the ion is not as yet certain; and it is a question whether it is a single charged molecule or a group of molecules about a charged molecule. For simplicity it is assumed here that it is merely a charged molecule of the gas.

Let an ion go an average path L in a time T, where T can be evaluated from $T = L/u$, u being the average velocity of thermal agitation of the molecules.

The distance S_t traversed by the ion in the direction of the field in virtue of its charge in a time T is given by

$$S_t = \frac{1}{2}aT^2 = \frac{1}{2}\frac{X\epsilon}{m}\frac{L^2}{u^2},$$

for $a = \frac{X\epsilon}{m}$, where ϵ is the charge, X the field strength and m the mass.

Now if the ion goes S_t in the direction of the field in T seconds its average velocity of drift in the field will be

$$\bar{v} = \frac{S_t}{T} = \frac{1}{2}\frac{X\epsilon}{m}\frac{L}{u}$$

or its mobility will be $K = \frac{\bar{v}}{X} = \frac{1}{2}\frac{\epsilon}{m}\frac{L}{u}$.

Now in this deduction the value of an average free path L was assumed and all paths were assumed to be equal. Actually, the paths are not all equal and in this case the assumption introduces a serious error, for the distance traversed during the time t is proportional to t^2. Thus, for a long path L, $t^2 = (x/u)^2$ would give a very different S_t than for a short path. The distribution of free paths must then be considered. Replacing T by t and L by x in the expression for S_t above,

$$S_t = \frac{1}{2}\frac{X\epsilon}{m}\frac{x^2}{u^2},$$

where x refers to all paths ending between x and $x + dx$. Now out of I initial paths the number of the length x is given by $-dy$ or $\frac{I}{L}e^{-\frac{x}{L}}dx$. Hence the average S_t is given by

$$\bar{S}_t = \frac{1}{2}\frac{X\epsilon}{m}\frac{\int_0^\infty \frac{x^2}{u^2}\frac{I}{L}e^{-\frac{x}{L}}dx}{I},$$

Whence $$\bar{S}_t = \frac{1}{2}\frac{X\epsilon}{m}\frac{1}{Lu^2}\left[-Lx^2e^{-\frac{x}{L}} + 2L\int xe^{-\frac{x}{L}}dx\right]_0^\infty$$

$$\bar{S}_t = \frac{X\epsilon}{2Lmu^2}[2L^3] = \frac{X\epsilon L^2}{mu^2}.$$

As the number of paths of an ion in going 1 cm is very great, the average time of a path may safely be taken as $t = T = L/u$; hence the expression for the velocity becomes

$$\bar{v} = \frac{\bar{S}_t}{\bar{T}} = \frac{X\epsilon L}{mu}$$

and the mobility is

$$K = \frac{\epsilon L}{mu},$$

in contrast to the value $K = \frac{1}{2}\frac{\epsilon}{m}\frac{L}{u}$ obtained in neglecting the distribution of free paths.

23. Experimental Knowledge of Molecular Free Paths.—The manner in which the free-path concept has been verified must for part of its details be postponed to Chap. VI, in which relations are deduced which involve the free path in such a form that it can be evaluated from experimental measurements. The relations involve the kinetic-theory deductions for the physical constants known as the coefficients of viscosity, of diffusion, and of heat conductivity of the gas. All these equations, although they have some uncertainty in the value of the numerical coefficients concerned in them, give nearly the same values for L. Again, the theory says that L should be related to σ, the diameter of the gas molecules, and to N, the number of molecules in a cm^3. In recent years σ has been determined[1] in a variety of ways and N has been accurately determined.[2] The values so obtained, in so far as they theoretically should agree, agree well with the values of L determined directly from viscosity.

The two best experimental proofs, however, depend on more direct measurements of the free paths and distribution of free paths. The first method is due to M. Born.[3] It depends on the measurement of the thickness of a silver film deposited on a glass plate out of a beam of silver atoms moving in an atmosphere of air at reduced pressures as a function of the distance x from the origin of the beam. The apparatus is schematically sketched in Fig. 8. From the small heated tip of the quartz tube A a stream of evaporating silver is reduced to a narrow beam by means of the tube B. From there the stream passed through a circular hole in each of four brass discs one above the other and 1 cm apart. These discs were cooled by liquid air about the upper portion of the quartz tube. Each of them supported a

glass quadrant P_1, P_2, P_3, or P_4 whose apex extended to the center of the circular opening. Each quadrant in turn was rotated through 90 deg. relative to the preceding one. Thus each of four cold glass screens at distances of 1 cm apart received one-fourth of the beam on their tips. The quartz tube was connected to an adequate pumping system and a set of gages for measuring and controlling the gas pressures was provided. The experiment then consisted in evaporating the silver at various pressures and measuring the relative amount of silver deposited on each plate as a function of the distance between the plates. The measurement was accomplished by a photometric comparison of the density of the deposits on the separate plates. The test of the theory by the experiments follows. If the equation for the distribution of free paths is correct, then the density of deposit should be given by

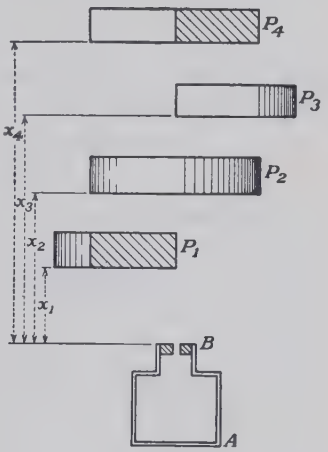

FIG. 8.

$$D = D_0 e^{-\frac{x}{L}},$$

where x is the distance between the plate and the origin B of the ray and L is the mean free path. In practice, however, even at the lowest pressures obtainable, there is a slight change in density on the different plates due to a geometrical spreading of the beam. Thus to eliminate this difficulty the measurements were made as follows: The values of the density D_{10} when there was no gas present and the free path had the length of the chamber, and the density D_1 on the same plate when the gas was present giving a free path L, are given by

$$D_1 = D_{10} e^{-\frac{x_1}{L}}$$

for one plate. For another one of the plates it is given by

$$D_2 = D_{20} e^{-\frac{x_2}{L}}$$

where x_1 and x_2 are the distances of the plates from the source (*i.e.*, the point B).

Therefore

$$L = \frac{x_2 - x_1}{\log\left(\frac{D_1}{D_2}\frac{D_{20}}{D_{10}}\right)}.$$

In the actual experiments reported, $x_2 - x_1 = 1$ cm. These gave in one series of measurements the following values:

for $p = 5.8 \times 10^{-3}$ mm, $L = 1.7$ cm.
$p = 4.5 \times 10^{-3}$ mm, $L = 2.4$ cm.

This gives pL constant within the limits of experimental error and so verifies the prediction of the kinetic theory. The values obtained for L if reduced to atmospheric pressure are then $L = 1.3 \times 10^{-5}$ and $L = 1.4 \times 10^{-5}$ cm. From viscosity measurements on L for air, the gas used here, $L = 0.99 \times 10^{-5}$ cm, while for Ag, which is a monatomic gas like Hg vapor, $L = 2 \times 10^{-5}$. Thus for the Ag atoms in air the value obtained by direct measurement is in excellent agreement with the other values, considering the difficulty of the experiment.

In a recent repetition of Born's experiment performed with great care, F. Bielz[4] has determined σ for collisions between silver atoms and N_2 molecules. The particular improvements in this work lay in the method of introducing the glass plates for catching the silver atoms, in the corrections for the spreading of the beam, and in the developing and measuring of the thickness of the deposit. In testing the law of distribution of paths, the free path L was calculated by means of the equation $D_x = D_0 e^{-\frac{x}{L}}$ from the measurements on the thickness of the deposit D_x at different values of x. The values of L multiplied by the pressures for different values of D should be constant. Three different values of x were used—22, 32, and 42 mm—and the following values for pL were obtained. 0.0132, 0.0104, 0.0097, 0.0109, 0.0094, 0.00945, with a mean of 0.0098. This degree of constancy, when considered in the light of the other experimental uncertainties, establishes the distribution law quite successfully. The value obtained for σ, the molecular diameter, is 2.58×10^{-8} cm, with an accuracy of 5 per cent. If $r = \frac{1}{2}\sigma$ for N_2 be taken as 1.55×10^{-8} cm, σ for the Ag atom is 1.0×10^{-8} cm.

24. Electron Free Paths.—In the preceding work the mean free path for gas molecules was deduced assuming molecules of diameter σ moving among like molecules. The value for L was

given by the expression $L = \frac{1}{\left(\frac{4}{3}\pi\sigma^2 N\right)}$, where σ is the diameter of the molecules, and the factor $\frac{4}{3}$ came in from a consideration of the relative velocities of the molecules. As will be seen later (Sec. 37, Chap. IV), if the distribution of the velocities be considered, the mean free path is given by the expression

$$L = \frac{1}{\sqrt{2}\pi\sigma^2 N},$$

where the $\sqrt{2}$ replaces the $\frac{4}{3}$ above. Now for an electron whose dimensions (3×10^{-13} cm) are minute compared to σ (2×10^{-8} cm) and whose velocity of agitation is much greater than that of the molecules, the equation may be simplified. For a point electron the sphere of exclusion has a radius $\sigma/2$ (*i.e.*, the radius of the molecules), for it can move right up to the surface of the assumed spherical molecules. Also the electron moves so much more rapidly than the molecules, since it has the same energy of agitation (as demanded by the law of equipartition) while it has less than $\frac{1}{3600}$ the mass of most molecules, that the latter can be considered at rest relative to it. Hence the correction for relative velocities may also be removed. The equation for the electron free paths L_1 therefore becomes

$$L_1 = \frac{1}{\pi(\sigma/2)^2 N}$$

and

$$L_1 = 4\sqrt{2}L.$$

25. Distribution of the Electron Free Paths.—It is possible to obtain a beam of electrons of almost any velocity and to shoot them through a gas. At any point of the gas the number of electrons can be measured and compared with the number at any other point by measuring, with an electrometer, the charges delivered by the electron beam per unit time in a Faraday cage. Now it also happens that electrons that are thrown out of the beam by colliding with molecules and being deflected by the impact, or those which have collided and lost appreciable velocities in the process, can be excluded from the measuring chamber. Thus it should be possible to measure y, the number of electrons which have escaped collision at any point of the path

x cm from the source, as a function of x. This would at once furnish an exceptional means of testing the distribution law.

The first man to test this was Lenard,[5] who even before his critical paper in 1903 had found that the number y of electrons at a distance x from the source moving in a beam in a gas at a pressure p could be accurately represented by an equation of the form

$$y = Ie^{-\alpha x}.$$

In this case α is a constant related to the free path L in a manner to be discussed later. This law he verified for a large range of pressures p and distances x. It holds well for electrons of velocities ranging from near that of light down to velocities of the order produced in electrons which have fallen through a potential difference of less than a volt. With varying velocities, however,

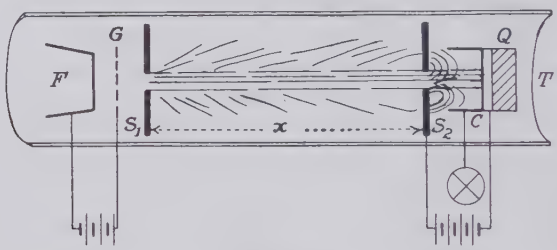

FIG. 9.

α, and hence the value of L, varies. The significance of this will be seen later.

More recently two men, H. F. Mayer[6] and C. Ramsauer[7] (later Brode[8] and others[11,12,13]), have carried on very refined measurements of this quantity at low velocities where the mean free paths of electrons should approach kinetic-theory values. The diagram of Mayer's experimental arrangement may be seen in Fig. 9. From the glowing filament F, electrons arise and are given a velocity v by means of the field between the gauze G and F. They then shoot in a nearly parallel beam through the small hole in the screen S_1. From there they traverse the gas space to a screen S_2 which is close to the Faraday cylinder C which is connected to the electrometer. The whole is placed in a glass tube T in which the gas pressure can be varied at will and accurately recorded. The distance x from C and S_2 to S_1 can be varied by moving C and S_2 back and forth by an electromagnet outside of the tube, C being attached to a small piece of soft iron Q. Between C and S_2 is

placed a retarding potential difference of about 0.95, of the initial potential driving the electrons from F to G. Thus if an electron having energy equivalent to the potential difference from F to G loses more than 5 per cent of its energy by impact with a molecule it will never be able to reach C against the field S_2C. For this apparatus the equation for y as a function of x, can be written as

$$y = f(x)I_0e^{-(a+\alpha p)x}$$

assuming that the experimental law of Lenard is correct. Here $f(x)$ is a small variation of the number of electrons with the distance x due to a spreading of the electron beam as a result of the mutual repulsion of the electrons. It is, on the whole, a function of the velocity of the electrons. The constant a is the constant for the absorption or scattering of the electrons by the residual gas in the apparatus when the pressure is at its lowest; α is the specific absorption of the gas and depends on the diameters of the molecules or, better, is a function of L; p is the gas pressure. Mayer in his experiment changed p and x and eliminated the factors $f(x)$, a, and I by four measurements. This was essential, as I changed some with the gas pressure due to cooling of the filament.

At a pressure p_1 the currents I_{11} and I_{12} were measured at distances x_1 and x_2, and at p_2 the currents I_{21} and I_{22} were measured for distances x_1 and x_2. Then

$$I_{11} = f(x_1)I_{10}e^{-(a+\alpha p_1)x_1},$$
$$I_{12} = f(x_2)I_{10}e^{-(a+\alpha p_1)x_2},$$
$$I_{21} = f(x_1)I_{20}e^{-(a+\alpha p_2)x_1},$$
$$I_{22} = f(x_2)I_{20}e^{-(a+\alpha p_2)x_2}.$$

$$\text{Call } \Delta_1 = \log \frac{I_{11}}{I_{12}}, \text{ and } \Delta_2 = \log \frac{I_{21}}{I_{22}},$$

whence

$$\alpha = \frac{\Delta_2 - \Delta_1}{(p_2 - p_1)(x_2 - x_1)}.$$

This gives the constant α per mm pressure if p_2 and p_1 are in millimeters, and per cm path difference if x_2 and x_1 are in centimeters. For a pressure p mm, "a" $= \alpha p$, where "a" is the constant of an equation giving the number of electrons which escape molecular encounters in going x cm in the gas. In its simple form, disregarding the correction terms for experimental difficulties above, the equation is

$$y = Ie^{-\text{“}a\text{”}\,x}$$

and comparing it with the free-path equation derived for molecules,

$$y = Ie^{-\frac{x}{L}},$$

it is seen that $\alpha p = \text{“}a\text{”} = 1/L_1$,

as
$$L_1 = \frac{1}{\pi\left(\frac{\sigma}{2}\right)^2 N} = \frac{1}{\text{“}a\text{”}}$$

$$\text{“}a\text{”} = \pi\left(\frac{\sigma}{2}\right)^2 N,$$

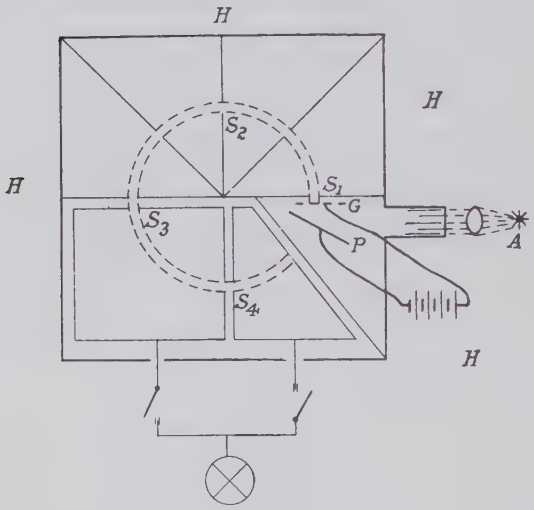

FIG. 10.

i.e., it is the total absorbing area, or area of cross-section, of the molecules in the volume in which there are N molecules. Thus the fact that “a”, and hence L_1, are constants for any gas independent of x and p establishes once and for all this relation and proves the legitimacy of the assumption of the distribution of free paths.

A method even more sensitive than this one is due to Ramsauer. In this case photoelectrons liberated from a plate P by light from an arc A are given a velocity by a field between a gauze G and the plate P. After passing through a slit S they are bent into a circular path by a uniform magnetic field H perpendicular to the plane of Fig. 10. By means of a series of narrow slits S_2, S_3, and

S_4, the electrons of one velocity are kept in the beam by the field; all others (*i.e.*, those having different curvatures) are screened out. Two insulated chambers corresponding to the third and fourth quadrants and bounded by the slits and S_3 and S_4 are connected so that they can have their charges read on two electrometers. Call x_3 and x_4 the distances from the screen S_1 to the screens S_3 and S_4. Call I_1 the current received by the fourth quadrant and i_1 the sum of the currents received by the third and fourth quadrants together at a pressure p_1. Call I_2 and i_2 the corresponding currents for a pressure p_2. Then from similar reasoning to that of Mayer

$$\alpha = \frac{1}{(p_2 - p_1)} \frac{1}{(x_4 - x_3)} \log \left(\frac{\frac{I_1}{i_1}}{\frac{I_2}{i_2}} \right).$$

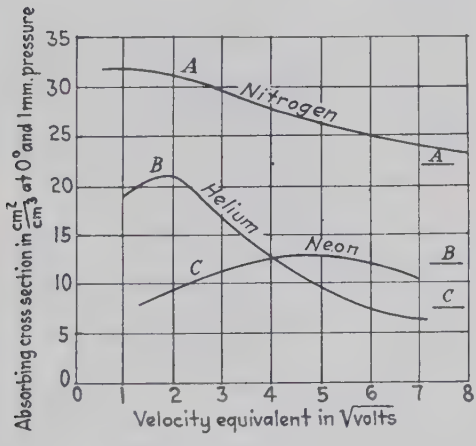

FIG. 11.

The chief difference between the two measurements is that, owing to the critical elimination due to the path of the rays in the field, only those electrons get through which have suffered practically no loss of energy or change in direction. The results agree for both methods well within the limits of error, when the velocities are low (*e.g.*, about 10 to 15 volts). By volt velocity is meant the equivalent potential through which an electron must fall freely to gain the velocity.

The curves obtained by Ramsauer for a number of gases are reproduced in Figs. 11 and 12, the quantities plotted are "a" per

mm pressure per cm^3 against the square root of the equivalent potential applied to give the electrons their speed. The values for "a" computed directly from "a" $= \frac{1}{4\sqrt{2}L}$, where L is obtained from viscosity measurements, are indicated by the straight lines on the right of the figure.

It is seen that in order of magnitude the values of "a" at the higher speeds are nearly the same as those for "a" computed from kinetic theory. For still higher speeds, "a" decreases rapidly as the velocity increases. This is easily explained, since it is only for lower speeds that the collisions of electrons with molecules are elastic and they are deflected by the surfaces of the molecules. At higher speeds the electrons begin to shoot through

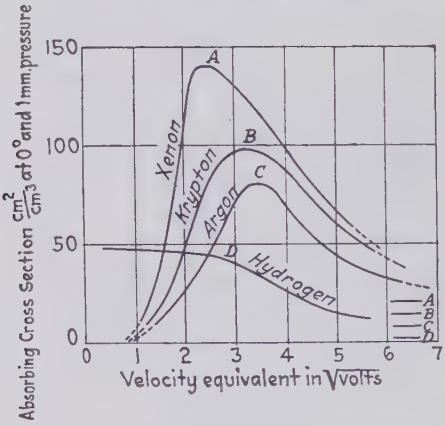

Fig. 12.

the molecules. The behavior at the lower velocities is nearly normal for all but the inert gases. At speeds near those exciting characteristic resonance effects in the electrons of the atoms or molecules themselves, the bombarding electrons, especially in the inert gases, seem to be much more readily deflected than otherwise. Thus the effective areas of the molecules are increased and the mean free paths fall to lower values. At still lower speeds the atoms of argon, neon, krypton, and xenon appear to become more transparent to electrons than the kinetic theory demands. In fact, the area for argon drops to one-fifteenth its kinetic-theory value at the lowest velocities, or the mean free path is multiplied by about 15. The meaning of this is obscure, and is characteristic of the peculiar symmetry of the inert gas atoms.

The other gases appear to show nearly normal free paths as the velocity decreases.

While the *particulate* explanation of the electron scattering by atoms, *i.e.*, the variation of the absorbing cross sections with electron velocity, is, to say the least, difficult and obscure, the new wave-mechanical analyses of these processes lead to a far more successful result. Thus in an interesting review of collision processes from the wave-mechanical point of view, P. M. Morse[14] in the *Reviews of Modern Physics* (page 583) gives the results of the wave-mechanical calculations of the absorbing cross sections of electrons in He, Ne, A, and Na as a function of velocity. The agreement obtained is really striking although in no way predictable on the classical theory.

Disregarding, however, the question of the detailed agreement involved in the accurate interpretation of these free paths which requires more powerful methods of analysis, it can be said that the study of electron free paths has generally confirmed the assumptions of the kinetic theory as to the distribution of the free paths and their magnitudes.

References

1. Hertzfeld, K. F.: *Jahrb. Radioakt. Elektronik*, **19**, 259, 1922.
2. Millikan, R. A.: "The Electron," University of Chicago Press, Chicago, 1917; 2d ed., Chicago, 1924.
3. Born, Max: *Phys. Z.*, **21**, 578, 1920.
4. Bielz, Fritz: *Z. Physik*, **32**, 81, 1925; also Gerlach, W.: Atomstrahlen, "Ergebnisse der Exakten Naturwissenschaften," vol. 3, p. 182, Julius Springer, Berlin, 1924.
5. Lenard, P.: "Quantitatives über Kathodenstrahlen aller Geschwindigkeiten," C. Winter, Heidelberg, 1918.
6. Mayer, H. F.: *Ann. Physik*, **64**, 451, 1921.
7. Ramsauer, Carl: *Ann. Physik*, **64**, 513, 1921; *Jahrb. Radioakt. Elektronik*, **19**, 345, 1922.
8. Brode, R. B.: *Phys. Rev.*, **25**, 636, 1925.
9. Clausius, R.: "Die Kinetische Theorie der Gase," Chap. II, F. Vieweg und Sohn, Braunschweig, 1889.
10. Clemens-Schaefer: "Einführung in die Theoretische Physik," vol. 2, part I, Sec. 85, p. 363, Berlin, 1921.
11. Rusch, M.: *Ann. Physik*, **80**, 707, 1926.
12. Kollath, R.: *Phys. Z.*, **31**, 986, 1930.
13. Brüche, E.: "Ergebnisse der Exakten Naturwissenschaften," vol. 8, p. 185, Julius Springer, Berlin, 1929.
14. Morse, P. M.: *Rev. Mod. Phys.*, **4**, 577, 1932.

Books Recommended

a. MEYER, O. E.: "Kinetic Theory of Gases," Chap. VI, Appendix III, Longmans, Green & Co., London, 1899.

b. CLAUSIUS, R.: "Die Kinetische Theorie der Gase," Chap. II, bound with "Die Mechanische Wärmetheorie," F. Vieweg und Sohn, Braunschweig, 1889.

c. JAEGER, G.: Winkelmann's "Handbuch der Physik," vol. 3, "Heat," chapter on Kinetic Theory, p. 693 ff., Johann Ambrosius Barth, Leipzig, 1906.

d. For a very complete summary on all determinations of molecular diameters containing a very good bibliography, emphasis must be laid on the excellent article by HERZFELD, K. F.: *Jahrb. Radioakt. Elektronik*, **19**, 259, 1922.

e. HERTZFELD, K. F.: "Kinetische Theorie der Wärme" (Section of Müller-Pouillet's "Lehrbuch der Physik"), Vieweg und Sohn, Braunschweig, 1925, Chap. Iα, Secs. 11–16.

f. HERTZFELD, K. F.: "Handbuch der Physik," edited by H. Geiger and K. Scheel, vol. 22, Chap. V, Secs. B, C, F, and G, Julius Springer, Berlin, 1926.

CHAPTER IV

THE DISTRIBUTION OF MOLECULAR VELOCITIES

26. Introduction.—Up to the present it has been assumed that all molecules moved with the same velocity. This assumption is, however, unjustified and it is incompatible with the assumed elasticity of the impacts of the gas molecules, as a little reflection will show. For simplicity, assume that all the molecules have equal masses and a common initial velocity c.* If the necessary assumption be made that the impacts are elastic (an assumption essential to the elementary kinetic concepts as otherwise the heat energy would go into the deformation of the molecules and would not remain as energy of translation), then out of the manifold types of collisions taking place the occurrence of an impact of the type pictured in Fig. 13 can be conceived. A molecule m_1 is moving with a velocity c_1. It is struck centrally by another molecule m_2 of the *same mass* moving at right angles to c_1 with an *equal* velocity c_2. After the impact, m_2 will have given all its velocity c_2 to m_1, which had no component parallel to c_2, for molecules in such an impact merely exchange velocities, as shown in Sec. 28. As a result, m_1 will now possess a velocity c_3 equal in magnitude to $\sqrt{2}c_1$ along the line indicated. m_2 will then have no velocity, while m_1 will have a velocity $\sqrt{2}c_1$. In this impact the *total energy* will be the same as before, for the

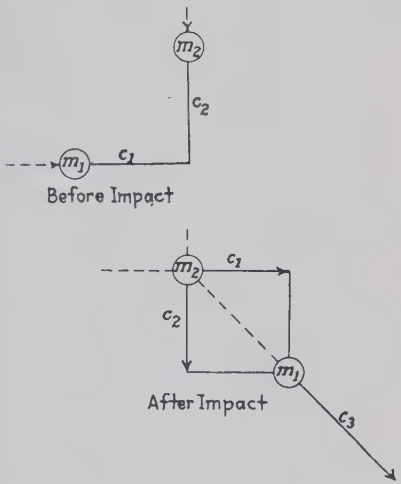

FIG. 13.

* Heretofore the velocity has been designated by the letter u. Since the recognition of the distribution of velocities, molecular velocities will be designated by the conventional symbol c.

initial energy was $\frac{1}{2}m_1c_1^2 + \frac{1}{2}m_2c_2^2 = m_1c_1^2$, since m_1 and c_1 have the same magnitudes as m_2 and c_2, and the final energy will be $\frac{1}{2}m_2(0)^2 + \frac{1}{2}m_1(\sqrt{2}c_1)^2 = m_1c_1^2$. Thus after the first impact in an extreme case, while the energy is conserved, the velocities of the two molecules will no longer be the same. For other impacts the changes will be less, but it is evident that even after a very few impacts the molecules will no longer have the same velocities, and, if enough molecules are taken, molecules with all sorts of velocities will exist. The average velocity $\sqrt{\bar{c}_1^2}$ will, however, remain the same, for $\frac{1}{2}m_1\bar{c}_1^2$ has been conserved, and as long as m_1 is constant c_1 must be constant. Thus the velocities will be distributed about an average value $\sqrt{\bar{c}_1^2}$ which depends, as will be seen, on the temperature of the gas only.

It will be the task of this chapter to deduce this law of distribution of velocities and to give what experimental evidence exists of its verification. The deductions given will be of two sorts.* The first one will be the general approach given by Boltzmann and based on a study of the equilibrium resulting in elastic impacts. The second one will be the original deduction due to Maxwell. In the latter case certain fundamental assumptions made about molecular motions and velocities are such that they fall into a category of *general conditions* in the theory of probabilities such that they lead to the deduction of the distribution law, which must therefore be the distribution law applicable to molecules.

27. Boltzmann's Method.†—The fundamental idea underlying this treatment is that a distribution arrived at from other considerations by Maxwell (Sec. 33), represents the equilibrium state after complete random motion has set in and the velocities have reached their permanent régime of velocities. If this is so, then the distribution law should follow from the condition that in elastic impact the number of molecules having velocities lying between certain limits is constant.

* Still another very ingenious elementary derivation is given in K. F. Hertzfelds, Kinetische Theorie der Wärme, Müller-Pouillets, Lehrbuch der Physik Vol. III, Part II, Chapter Iα, Sect. 7.

† The treatment given here is not a translation of Boltzmann's original deduction.[18] It is a free translation of the very admirable and condensed version of it given by Clemens-Schaefer in his splendid book, "Einführung in die Theoretische Physik."[19]

Let it be assumed that the molecules are rigid elastic spheres and consider those molecules having velocity components between u and $u + du$, v and $v + dv$, and w and $w + dw$, where u, v, and w represent the velocities along the x-, y-, and z-axes. Geometrically considered, these may be represented as those molecules for which the velocity vectors drawn from a point O in Fig. 14 all end in the small volume element $dudvdw$. Assuming that a distribution law exists and that there are n molecules all told, the number ending in $dudvdw$ can be written as $nf(u, v, w)\, dudvdw$. Here $f(u, v, w)$ represents the function expressing the Maxwellian distribution which it is desired to find. For the sake of brevity let these particular molecules be known as molecules of type A. Per unit volume there are $Nf(u, v, w)\, dudvdw$ of these, where N is the total number of molecules per cm^3. As molecules of type B such molecules may be considered as have velocities lying in a volume element $du'dv'dw'$, *i.e.*, with velocities between u' and $u' + du'$, v' and $v' + dv'$, and w' and $w' + dw'$. The number of molecules of the type B per unit volume is, similarly,

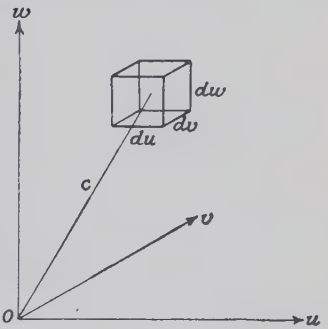

Fig. 14.

$$Nf(u', v', w')du'dv'dw'.$$

The molecules which were at a given instant of type A before an impact change their velocities in a time interval dt as a result of the impacts, while in the same time interval more molecules of other classes as result of impacts enter the type A. *Between these two changes at equilibrium in the gas, an equilibrium must exist, and it is this equilibrium which will define the distribution law.*

One may begin by considering those impacts in virtue of which the *A-type molecules are decreased in number.* Of these impacts it is perhaps simpler not to consider those with all types of molecules and A molecules, but only those between the type-A molecules and the type-B molecules. Impacts between the A- and B-type molecules may now be discussed with an added restriction, namely, that at the instant of impact the lines of centers of the molecules (taken from A to B) have a definite orientation in space. As, however, the A and B molecules have vectors which

end in a finite though small volume ($dudvdw$), the directions of the lines of centers will vary within certain small limits also, that is, the direction cosines of the line of centers is restricted so as to have components which lie between l and $l + dl$, m and $m + dm$, and n and $n + dn$. If these lines of center were to be depicted as drawn from a common origin, they would for the collisions considered cut out a small surface element dK in a unit sphere drawn about the origin (see Fig. 15). Such collisions will be termed the collisions of type α. To simplify still further the letter F may be written for the product N times the function f. Thus the number of molecules of types A and B per unit volume is given by $F(uvw)dudvdw$ and $F(u'v'w')$ $du'dv'dw'$. And the number of impacts of A molecules with B molecules of the class α in the time dt is given by $\nu_\alpha dt = F(uvw)\ F(u'v'w')\delta^2 c_r \cos \theta dK dudvdw\ du'dv'dw'dt$. This results from a consideration of the nature of the impacts of the molecules considered as spheres. If the molecules have the diameter δ, an impact occurs every

Fig. 15.

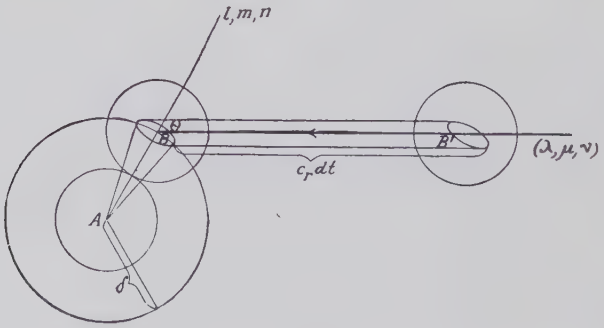

Fig. 16.

time that the length of the line of centers takes on the value δ. In Fig. 16, call A the center of the A molecule and describe a circle of radius equal to the molecular diameter δ about it. An impact then occurs when the center of the B molecule lies on this circle.

In particular, this will be an impact of the α type if the direction $\overrightarrow{AB}$ has the direction cosines l, m, n.

Since dK is the surface cut out of unit sphere by the impacts (i.e., the solid angle), these same impacts will cut out of the sphere of radius δ a surface element $\delta^2 dK$. The cone filled by the lines of centers in all the α impacts is shown in the figure. The question now is, How many of the B molecules will collide with A molecules in the time dt? This does not depend on the absolute velocities of the A and B molecules but on their relative velocities. The A molecules may then be considered fixed and the B molecules moving towards them with a velocity c_r. This direction of relative velocity is, obviously, the direction of the straight line $\overrightarrow{B'B}$ and has the direction cosines $\frac{u'-u}{c_r}, \frac{v'-v}{c_r}, \frac{w'-w}{c_r}$, which will be called λ, μ, ν for simplicity. If now there is constructed about $B'B$ as axis an oblique cylinder whose base is the surface element $\delta^2 dK$ and whose length is $B'B$, then in the time dt only those B molecules which lie in the cylinder will collide with the A molecules. Since $B'B$ is equal to $c_r dt$, the volume of this cylinder will be $\delta^2 dK c_r \cos\theta dt$, where, from the figure, $\cos\theta$ is equal to $-(\lambda l + m\mu + n\nu)$. The negative sign comes from the fact that $l\lambda + m\mu + n\nu$ is equal to the cosine of the supplementary angle of θ, and the cosine of the obtuse supplementary angle is negative. Since the volume must be positive, the negative sign must be included in the term for the volume. As per unit volume there are $F(u'v'w')du'dv'dw'$ molecules of the type B, the cylinder contains

$$F(u'v'w')\ \delta^2 c_r \cos\theta dK du'dv'dw'dt$$

molecules. These and only these molecules undergo the α-type collisions with the A molecules in the time dt.

Now there are in a unit volume $F(uvw)\,dudvdw$ of the A type of molecules present, so that in the time dt the number of impacts of the α type occurring, $\nu_\alpha dt$, will be given by

$$\nu_\alpha dt = F(uvw)\,F(u'v'w')\,\delta^2 c_r \cos\theta dK dudvdwdu'dv'dw'dt.$$

If, for simplicity, $F(uvw)$ and $F(u'v'w')$ be written merely F and F', then the decrease in the number of A molecules per cm^3 in a time dt through α collisions is given by

$$FF'\delta^2 c_r \cos\theta dK dudvdwdu'dv'dw'dt.$$

It is next necessary to determine the increase in the number of A molecules per unit volume in the time dt. To this end another

special type of impacts, which may be termed β impacts, must be regarded. These impacts are defined by the following three conditions:

1. After the impact *one* of the two molecules must belong to type A, that is, its velocity as a result of the impact must lie in the volume element $dudvdw$ of the velocity space.

2. After the impact the second molecule must belong to the type B, that is, its velocity as a result of the impact must lie in the volume element $du'dv'dw'$.

3. At the instant of impact the line of centers should have the direction cosines l, m, n, that is, it must go through the element dK of the unit sphere (Fig. 15). In this case the velocities *after impact* are defined. *It is now necessary to calculate on the basis of the laws of elastic impact the velocities* u, v, w *and* u', v', w' of *these molecules before they collided.* This is accomplished by an analysis of elastic impacts which follows.

28. Velocity Exchanges in Elastic Impacts.—Between two rigid molecules of equal masses two types of impacts may occur. The simpler of the two could be termed "head-on collisions," that is, collisions in which the direction of motion coincides with the line of centers at impact. The second type of impact may be termed "oblique impacts," and are such that the direction of motion and the line of centers at impact do not coincide. From the simple laws of impact for the first case the impacts in the second case may be deduced to the extent to which they concern the type of collisions for which they will be used.

Consider two molecules A and B which possess before impact the velocities c and c' along the same line. Let their velocities after impact be $\bar{c}$ and $\bar{c}'$. From the conservation of energy, since the masses are equal, it is possible to write

$$c^2 + c'^2 = \bar{c}^2 + \bar{c}'^2,$$

and from the law of conservation of momentum,

$$c + c' = \bar{c} + \bar{c}'$$

If these equations are written in the following form:

$$c^2 - \bar{c}^2 = \bar{c}'^2 - c'^2$$

$$c - \bar{c} = \bar{c}' - c'$$

division of the first by the second equation yields

$$c + \bar{c} = c' + \bar{c}'.$$

Combining this equation with $c - \bar{c} = \bar{c}' - c'$,

the result is

$$\bar{c} = c'$$

$$\bar{c}' = c$$

that is, the two molecules have merely exchanged velocities. Consider next the more complicated case in which the velocities C and C', which now must be considered as vectors, have directions differing from each other as well as from the line of centers AB of Fig. 17. C and C' may be decomposed into two components each, one parallel to the line of centers and the other perpendicular to it. Expressed in another way, C and C' may be decomposed into two vectors C_t and C'_t parallel to the common tangential plane at the instant of impact, and C_n and C'_n normal to this plane. For smooth spheres the tangential components

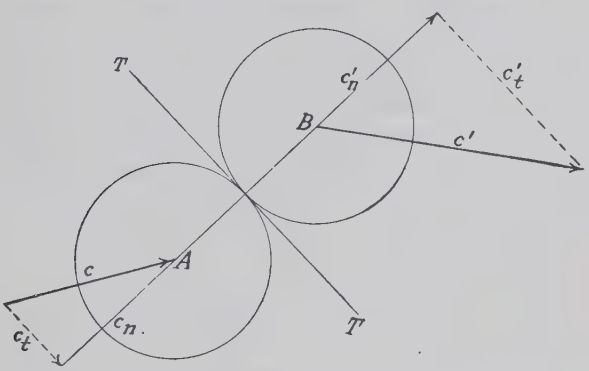

FIG. 17.

C_t and C'_t remain unchanged after the impact, while the normal components play the same rôle as in head-on impacts. If the velocity components after collision be designated, as $\overline{C}_t$, $\overline{C}'_t$ and $\overline{C}_n$ $\overline{C}'_n$, corresponding to the components C_t, C'_t and C_n and C'_n before impact, these facts may be expressed by writing

$$\left.\begin{aligned}\overline{C}_t &= C_t \\ \overline{C}'_t &= C'_t\end{aligned}\right\} \tag{1}$$

and

$$\left.\begin{aligned}\overline{C}_n &= C'_n \\ \overline{C}'_n &= C_n\end{aligned}\right\}. \tag{2}$$

Since vectorially expressed

$$C = C_t + C_n,$$

Eqs. (1) and (2) above lead to the following relations:

$$\begin{aligned}C &= C_t + C_n = \overline{C}_t + \overline{C}'_n \\ C' &= C'_t + C'_n = \overline{C}'_t + \overline{C}_n\end{aligned} \tag{3}$$

These may be expressed somewhat differently if the relative vector $\overline{C}_r$ after impact be used, where

$$\overline{C}_r = \overline{C}' - \overline{C}. \tag{4}$$

Since vectorially expressed $\bar{C}_t = \bar{C} - \bar{C}_n$, Eq. (3) becomes

$$C = \bar{C} - \bar{C}_n + \bar{C}'_n = \bar{C} + (\bar{C}' - \bar{C})_n$$

or, using Eq. (4),

$$C = \bar{C} + (\bar{C}_r)_n. \tag{5}$$

Here $(\bar{C}_r)_n$ signifies the normal component of the relative velocity. In a similar way from Eqs. (3) and (4):

$$\begin{aligned} C' &= \bar{C}'_t + \bar{C}_n = \bar{C}'_t + (\bar{C}_n - \bar{C}'_n) + \bar{C}'_n \\ &= \bar{C}'_t + \bar{C}'_n - (\bar{C}_r)_n, \end{aligned}$$

and since $\bar{C}'_t + \bar{C}'_n = \bar{C}'$,

$$C' = \bar{C}' - (\bar{C}_r)_n. \tag{6}$$

Equations (5) and (6) may be written in terms of their components along the three coordinate axes. Call the components of the velocity C, u, v, and w, and similarly for the other velocities, adding the proper subscripts. Furthermore, call the direction cosines of $(\bar{C}_r)_n$ the normal component of the relative velocity (this is, the same as the direction of the line of centers), l, m, n. Then according to Eq. (5)

$$\left.\begin{aligned} u &= \bar{u} + l \cdot (\bar{C}_r)_n \\ v &= \bar{v} + m \cdot (\bar{C}_r)_n \\ w &= \bar{w} + n \cdot (\bar{C}_r)_n \end{aligned}\right\}, \tag{7}$$

and according to Eq. (6)

$$\left.\begin{aligned} u' &= \bar{u}' - l \cdot (\bar{C}_r)_n \\ v' &= \bar{v}' - m \cdot (\bar{C}_r)_n \\ w' &= \bar{w}' - n \cdot (\bar{C}_r)_n \end{aligned}\right\}. \tag{8}$$

Again, according to the definition of the relative velocity $\bar{C}_r$ the direction cosines of the normal component of the latter are

$$l = \frac{\bar{u}' - \bar{u}}{(\bar{C}_r)_n}, \; m = \frac{\bar{v}' - \bar{v}}{(\bar{C}_r)_n}, \; n = \frac{\bar{w}' - \bar{w}}{(\bar{C}_r)_n}.$$

Multiplying these equations in sequence by l, m, and n, the result is, since $l^2 + m^2 + n^2 = 1$,

$$(\bar{C}_r)_n = (\bar{u}' - \bar{u})l + (\bar{v}' - \bar{v})m + (\bar{w}' - \bar{w})n. \tag{9}$$

Putting these into Eqs. (7) and (8) the results are:

$$\left.\begin{aligned} u &= \bar{u} + l^2(\bar{u}' - \bar{u}) + lm(\bar{v}' - \bar{v}) + ln(\bar{w}' - \bar{w}) \\ v &= \bar{v} + lm(\bar{u}' - \bar{u}) + m^2(\bar{v}' - \bar{v}) + mn(\bar{w}' - \bar{w}) \\ w &= \bar{w} + ln(\bar{u}' - \bar{u}) + mn(\bar{v}' - \bar{v}) + n^2(\bar{w}' - \bar{w}) \end{aligned}\right\} \tag{10}$$

and

$$\left.\begin{aligned} u' &= \bar{u}' + l^2(\bar{u} - \bar{u}') + lm(\bar{v} - \bar{v}') + ln(\bar{w} - \bar{w}') \\ v' &= \bar{v}' + lm(\bar{u} - \bar{u}') + m^2(\bar{v} - \bar{v}') + mn(\bar{w} - \bar{w}') \\ w' &= \bar{w}' + ln(\bar{u} - \bar{u}') + mn(\bar{v} - \bar{v}') + n^2(\bar{w} - \bar{w}') \end{aligned}\right\} \tag{11}$$

These expressions give the components of velocity uvw and $u'v'w'$ before the impact in terms of $\bar{u}\bar{v}\bar{w}$ and $\bar{u}'\bar{v}'\bar{w}'$ after impact, and *vice versa*.

29. Continuation of the Boltzmann Derivation of the Distribution Law.—The equations deduced from the velocity exchanges in elastic impacts make it possible to calculate at once the desired velocity components before the impact. It must, however, be remembered that the quantities which it is required to find and which were expressed by $\bar{u}\bar{v}\bar{w}$ and $\bar{u}'\bar{v}'\bar{w}'$ in the first part of this deduction correspond to the quantities uvw and $u'v'w'$ of the section on Velocity Exchanges. Thus the quantities that have dashes over them in the *velocity exchange deduction* become the undashed quantities in this case, and *vice versa*. For example, according to Eq. (10) of the preceding section, for the velocity components $\bar{u}\bar{v}\bar{w}$ of the molecules which after impact will fall into type A, the following values are found:

$$\begin{aligned}\bar{u} &= u - \{l^2(u - u') + lm(v - v') + ln(w - w') \ \}\cdot \\ \bar{v} &= v \ - \{lm(u - u') + m^2(v - v') + mn(w - w')\}\cdot \\ \bar{w} &= w - \{ln(u - u') + mn(v - v') + n^2(w - w') \ \}\cdot\end{aligned}$$

And for the velocity components $\bar{u}'\bar{v}'\bar{w}'$ of the molecules which after impact will belong to the B type of molecules, from Eq. (11) of the preceding section the following values are found:

$$\begin{aligned}\bar{u}' &= u' - \{ \ l^2(u' - u) + lm(v' - v) + ln(w' - w)\}\cdot \\ \bar{v}' &= v' \ - \{lm(u' - u) + m^2(v' - v) \ + mn(w' - w)\}\cdot \\ \bar{w}' &= w' - \{ln(u' - u) + nm(v' - v) + n^2(w' - w)\}\cdot\end{aligned}$$

From analogy to the considerations for the number of impacts in dt which removed A-type molecules from the class by α impacts the number of impacts between these molecules *leading to the formation of A and B molecules* per unit volume in dt is given by $F(\bar{u}\bar{v}\bar{w})F(\bar{u}'\bar{v}'\bar{w}')(\delta^2 c_r \cos\theta dK d\bar{u}d\bar{v}d\bar{w}d\bar{u}'d\bar{v}'d\bar{w}'dt)$. This expression is the exact analogue of the previous expression for the disappearance of A molecules, and may be written

$$\bar{F}\bar{F}'\delta^2 c_r \cos\theta dK d\bar{u}d\bar{v}d\bar{w}d\bar{u}'d\bar{v}'d\bar{w}'dt.$$

These are, however, not necessarily β impacts but can only be so if the quantities $d\bar{u}$, $d\bar{v}$, $d\bar{w}$, $d\bar{u}'d\bar{v}'d\bar{w}'$ are so determined that $\bar{u} + d\bar{u}$, etc., *before* the impact go over into $u + du$, etc. *after* the impact, for a β impact is so defined that the molecule must go into the A type (having velocities between u and $u + du$, etc.) *after* the impact—that is, not only must $\bar{u}\bar{v}\bar{w}$ go over into u, v, and w after the impact, but $\bar{u} + d\bar{u}$, $\bar{v} + d\bar{v}$, and $w + d\bar{w}$ must go

over into $u + du$, $v + dv$, and $w + dw$. In order that this may occur, $d\bar{u}$, $d\bar{v}$, $d\bar{w}$, $d\bar{u}'$, $d\bar{v}'$, $d\bar{w}'$ must be so determined that they correspond to the quantities du, dv, dw, du', dv', dw' after impact. The quantities $d\bar{u}$, . . . $d\bar{w}'$ must be determined by differentiation of the equations giving $\bar{u}$, . . . $\bar{w}'$ in terms of u, . . . w' above. Differentiating thus,

$$d\bar{u}d\bar{v}d\bar{w} \cdot d\bar{u}'d\bar{v}'d\bar{w}' = \Delta dudvdw \cdot du'dv'dw'$$

is obtained, where Δ is the substitution determinant.

$$\Delta = \begin{vmatrix} \frac{\partial\bar{u}}{\partial u}, & \frac{\partial\bar{u}}{\partial v}, & \frac{\partial\bar{u}}{\partial w}, & \frac{\partial\bar{u}}{\partial u'}, & \frac{\partial\bar{u}}{\partial v'}, & \frac{\partial\bar{u}}{\partial w'} \\ \frac{\partial\bar{v}}{\partial u} & & & & & \frac{\partial\bar{v}}{\partial w'} \\ \frac{\partial\bar{w}}{\partial u} & & & & & \frac{\partial\bar{w}}{\partial w'} \\ \frac{\partial\bar{u}'}{\partial u} & & & & & \frac{\partial\bar{u}'}{\partial w'} \\ \frac{\partial\bar{v}'}{\partial u} & & & & & \frac{\partial\bar{v}'}{\partial w'} \\ \frac{\partial\bar{w}'}{\partial u} & & & & & \frac{\partial\bar{w}'}{\partial w'} \end{vmatrix}$$

The coefficients of these come from the equations for $\bar{u}\bar{v}\bar{w}$ and $\bar{u}'\bar{v}'\bar{w}'$ and it is seen that Δ is given by

$$\Delta = \begin{vmatrix} 1 - l^2, & -lm, & -ln, & l^2, & lm, & ln \\ -lm, & 1 - m^2, & -mn, & lm, & m^2, & mn \\ -ln, & -mn, & 1 - n^2, & ln, & mn, & n^2 \\ l^2, & lm, & ln, & 1 - l^2, & -lm, & -ln \\ lm, & m^2, & mn, & -lm, & 1 - m^2, & -mn \\ ln, & mn, & n^2, & -ln, & -mn, & 1 - n^2 \end{vmatrix}.$$

Evaluation of this determinant yields the result that $\Delta = +1$. Hence $d\bar{u}d\bar{v}d\bar{w} \cdot d\bar{u}'d\bar{v}'d\bar{w}' = dudvdw \cdot du'dv'dw'$. This equation is a special case of a famous theorem of Liouville. It is therefore found that if the velocity vectors of two molecules before an impact be in definite volume elements of the velocity space, they will after impact lie in different volume elements, which, however, are of the same size as the initial elements.

Thus the equation for the formation of A molecules from β impacts takes on the form

$$\bar{F}\bar{F}'\delta^2 c_r \cos\theta dK dudvdw \cdot du'dv'dw' \cdot dt.$$

The net increase of the A-type molecules in unit volume through impacts of the α and β type in the time dt is, therefore,

$$(\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta dK du dv dw du' dv' dw' \cdot dt.$$

By integration over all values of $u'v'w'$ as well as all values of dK, the increase in the number of A molecules in unit volume in the time dt through all possible impacts, is obtained, to wit

$$du dv dw \cdot dt \int\int\int\int (\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta dK du' dv' dw'$$

Now the number of molecules of type A was assumed to be $F(uvw)dudvdw$ at the beginning of the discussion. This number in the time dt changes to

$$\left(F + \frac{\partial F}{\partial t} dt\right) dudvdw.$$

Hence the increase in the number of A-type molecules per unit volume in a time dt is expressed by

$$\frac{\partial F}{\partial t} dt \cdot dudvdw.$$

Accordingly,

$$\frac{\partial F}{\partial t} = \int\int\int\int (\bar{F}\bar{F}' - FF')\delta^2 \cdot c_r \cos\theta \cdot du' dv' dw' dK.$$

From this equation it follows that the relation

$$\bar{F}\bar{F}' - FF' = 0$$

is a *sufficient* condition that $\partial F/\partial t = 0$, that is to say, it is a sufficient condition that a stationary state has been reached. It does not prove that it is a necessary condition, for in order to make $dF/dt = 0$ it is only necessary that the integral as a whole vanish. This will occur if $\bar{F}\bar{F}' - FF'$ is equal to 0. It will also occur if the quantity $\bar{F}\bar{F}' - FF'$ has *positive* and *negative* values such that the integration carried out between the limits makes the integral vanish. If it could be shown that $\bar{F}\bar{F}' - FF'$ is always positive or always negative, the condition $\bar{F}\bar{F}' - FF' = 0$ would be both a sufficient and a necessary condition that the integral vanish.

The condition, however, that $\partial F/\partial t = 0$ is sufficient to determine the distribution law. If it is brought to vanish through $\bar{F}\bar{F}' - FF'$ being zero, the distribution law evaluated by this condition would be a possible distribution law. In order to

show that it is the *only* distribution law, the condition that $\overline{FF}' - FF' = 0$ would have to be proved to be the *necessary* and *sufficient* condition for $\partial F/\partial t$ becoming 0. This was accomplished by Boltzmann by means of his famous H theorem.

30. Application of the H Function.—To prove that $\overline{FF}' - FF'$ is always of one sign in the integration, Boltzmann studied the so-called H function, or logarithmic function,

$$H = \int\int\int F \log F du dv dw,$$

in which the integration is to be carried out over all possible values of u, v, and w, *i.e.*, from $-\infty$ to $+\infty$. H is thus a pure number entirely independent of u, v, and w, and dependent only on the analytic form of F. Now in equilibrium F is not supposed to change with time, that is, the function represented by F is the one expressing the equilibrium condition. Thus the condition of equilibrium may be expressed by writing that $dH/dt = 0$, for if F is a constant with respect to time the derivative of $\int\int\int F \log F du dv dw$ with respect to t must be 0.

It is next necessary to determine dH/dt relative to the quantities which have been dealt with. Differentiating $F \log F du dv dw$ under the integral sign,

$$\frac{dH}{dt} = \int\int\int \left(\frac{dF}{dt} + \frac{dF}{dt} \log F\right) du dv dw.$$

Putting in the value of dF/dt obtained for the increase in A molecules above, the expression

$$\frac{dH}{dt} = \int\int\int\int\int\int\int\int (1 + \log F)\ (\overline{F}\overline{F}' - FF')\delta^2 c_r \cos\theta du \ \ldots \ dw' dK$$

is obtained. Now so far the A molecules only have been emphasized, inasmuch as it was desired to determine their increase in number. Actually, the B molecules also change, and since the B molecules are in no way subordinate to A molecules in these processes their changes must be included in the calculations. In fact, the division of molecules into A and B types was, in reality, only a mathematical convenience for simplifying the discussion. Thus there must exist for the B molecules a set of equations analogous to those for the A molecules in which the

accented letters are merely substituted for the unaccented letters, to wit

$$\frac{\partial F'}{\partial t} = \int\int\int\int (\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta du dv dw dK$$

and

$$H = \int\int\int F' \log F' du' dv' dw'.$$

These two lead to an equally justified value for dH/dt, namely,

$$\frac{dH}{dt} = \int\int\int\int\int\int\int (1 + \log F')\ (\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta du \ldots dw' dK.$$

Addition of these two expressions for dH/dt and division by 2 lead to an average value for dH/dt, in which both collisions are equally regarded. This value takes the form

$$\frac{dH}{dt} = \frac{1}{2}\int\int\int\int\int\int\int (2 + \log FF')\ (\bar{F}\bar{F}' - FF')\ \delta^2 c_r \cos\theta du \ldots dw' dK.$$

This value again, however, considers only the α type of impacts, since the α type of impacts was taken as the starting point of the discussion. Since the β collisions could have been used as the starting point as well as the α, they must be included in the evaluation of a final neutral value of dH/dt. Thus two expressions can be gained analogous to those just averaged which would follow if the β impacts had been used as the starting point. These are obtained again by merely interchanging the dashed and undashed letters for dF/dt and dF'/dt used before and for the H used before. If this transformation is carried out, the effect of the use of the β type of impacts as a starting point leads to the expression

$$\frac{dH}{dt} = -\frac{1}{2}\int\int\int\int\int\int\int (2 + \log \bar{F}\bar{F}')\ (\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta du \ldots dw' dK,$$

in which, because of the relation $du \ldots dw' = d\bar{u} \ldots d\bar{w}'$ the dashes were left off in the final differential product. Averaging this expression for dH/dt with the one based on the α impacts as a starting point, the perfectly symmetrical expression for dH/dt below is obtained:

$$\frac{dH}{dt} = \frac{1}{4}\int\int\int\int\int\int\int (\log FF' - \log \bar{F}\bar{F}')\ (\bar{F}\bar{F}' - FF')\delta^2 c_r \cos\theta du \ldots dw' dK.$$

This integrand is always negative since $\bar{F}\bar{F}' - FF'$ has the opposite sign from $\log FF'/\bar{F}\bar{F}'$, while all other quantities are positive, for θ is always less than $\frac{\pi}{2}$. Since the integrand is always negative or equal to zero, integration between no limits whatever can make the integral vanish. Thus the integral can be 0 only if the integrand $\bar{F}\bar{F}' - FF'$ is 0.

31. Conclusion of Boltzmann's Method.—Since, therefore, the condition that $dH/dt = 0$ is synonymous with the state of equilibrium, equilibrium will occur *only* when

$$\bar{F}\bar{F}' - FF' = 0.$$

This condition is, accordingly, also the necessary condition for equilibrium. Thus the equilibrium condition is defined by $\bar{F}\bar{F}' - FF' = 0$ and by its means the form of the distribution law may be determined.

To arrive at this from the above equation it is simpler to divide the equation by N, the number of molecules per unit volume, and one has the equation in the form,

$$\bar{f}\bar{f}' - ff' = 0, \text{ where } \bar{f}, \bar{f}', f, f' \text{ express } \frac{\bar{F}}{N}, \frac{\bar{F}'}{N}, \frac{F}{N}, \frac{F'}{N}.$$

Furthermore, since for equilibrium all directions in space are equivalent, therefore the f's depend on the magnitudes *of the velocities only* and not on the directions. This may be expressed by the equations

$$\begin{aligned} f &= e^{\phi(c^2)} \\ f' &= e^{\phi(c'^2)} \\ \bar{f} &= e^{\phi(\bar{c}^2)} \\ \bar{f}' &= e^{\phi(\bar{c}'^2)}, \end{aligned}$$

for the letter c represents the appropriate vector velocities of the molecules in the A, B, α, and β impact classes. The square is used to make them independent of the sign of the velocity.

From the law of conservation of energy one can write

$$c^2 + c'^2 = \bar{c}^2 + \bar{c}'^2$$

hence

$$\bar{c}^2 = c^2 + c'^2 - \bar{c}'^2.$$

Putting $\bar{f}\bar{f}' - ff' = 0$ into logarithmic form

$$\log \bar{f} + \log \bar{f}' - \log f - \log f' = 0,$$

and substituting the values for $\bar{f}, \bar{f}', f$ and f' assumed above, one obtains

$$\phi(\bar{c}^2) + \phi(\bar{c}'^2) - \phi(c^2) - \phi(c'^2) = 0.$$

Substituting for $\bar{c}^2$, this becomes $\phi(c^2) + \phi(c'^2) = \phi(\bar{c}'^2) + \phi(c^2 + c'^2 - \bar{c}'^2)$.

Differentiating this partially with respect to c^2, c'^2, and $\bar{c}'^2$ respectively, one obtains*

$$\begin{aligned} \phi'(c^2) &= \phi'(c^2 + c'^2 - \bar{c}'^2) \\ \phi'(c'^2) &= \phi'(c^2 + c'^2 - \bar{c}'^2) \\ \phi'(\bar{c}'^2) &= \phi'(c^2 + c'^2 - \bar{c}'^2) \end{aligned}$$

or $$\phi'(c^2) = \phi'(c'^2) = \phi'(\bar{c}'^2).$$

Such an equation can hold only if the derivatives are equal to a constant which one may call $-1/\alpha^2$, *i.e.*, if

$$\phi'(c^2) = -\frac{1}{\alpha^2}.$$

Integrating this and calling $\log A^3$ a constant of integration,

$$\phi(c^2) = -\frac{1}{\alpha^2} c^2 + \log A^3,$$

that is, it can hold only if

$$f = e^{\phi(c^2)} = A^3 e^{-\frac{c^2}{\alpha^2}}.$$

But f is the abbreviation of $f(u, v, w)$, and $c^2 = u^2 + v^2 + w^2$, so that

$$f(u, v, w) = A^3 e^{-\frac{1}{\alpha^2}(u^2 + v^2 + w^2)}$$

or, separately, $f(u) = Ae^{-\frac{u^2}{\alpha^2}}$, $f(v) = Ae^{-\frac{v^2}{\alpha^2}}$, and $f(w) = Ae^{-\frac{w^2}{\alpha^2}}$.

If there are N molecules present in a cm^3 the numbers having velocities between u and $u + du$, v and $v + dv$, and w and $w + dw$ are given by $N_{du} = Nf(u)du = ANe^{-\frac{u^2}{\alpha^2}}du$, $N_{dv} = ANe^{-\frac{v^2}{\alpha^2}}dv$, and $N_{dw} = ANe^{-\frac{w^2}{\alpha^2}}dw$.

This is the expression indicating the distribution of velocities. The physical meaning of the constants A and α will be determined in the treatment of the distribution law as deduced by Maxwell (Secs. 34 and 35).

32. The H Theorem and the Meaning of H.—The significance of the quantity H is far more extensive than a mere aid to the determination of the distribution law, for it makes it possible to obtain a mechanical significance for an otherwise difficultly interpretable quantity, namely, the entropy. It is, however, beyond the scope of this text to derive the relationship or to enter into the more recent rigorous proofs of the H theorem. This falls into the domain of statistical mechanics.

*The prime over the ϕ, *i.e.*, ϕ', designates the derivative of ϕ.

It was noticed that the integrand in the expression for dH/dt was always negative and in the limiting case of equilibrium 0. Thus for every case deviating from the stationary state one obtains the inequality

$$\frac{dH}{dt} < 0$$

and *only* for the stationary state does one obtain the equation $dH/dt = 0$. These two statements constitute the Boltzmann H theorem in its simplest form. Its significance consists in the following:

Thermodynamics teaches that an isolated system can successively take on only such states that its entropy always increases. If the entropy can no longer increase the system remains in a state of equilibrium which is defined by this fact. Thus entropy as a function of time follows the inequality that $dS/dt \geqq 0$; the negative entropy will consequently be represented by the relation $-dS/dt \leqq 0$, which is completely analogous to the inequality for H. Thus it is expected that H must be closely related to negative entropy. Since H has a purely mechanical definition, a mechanical definition of entropy is reached. In fact, it can be shown by analysis[31] that for a monatomic gas in equilibrium the entropy, aside from certain constants of integration, is related to the quantity H by the relation

$$S = -\frac{R}{N_A}H = -kH$$

where R is the universal gas constant and N_A is the Avogadro number. A still further analysis leads to the interesting result that H is the negative logarithm of the thermodynamic probability. This thermodynamic probability is, in turn, the number of equally probable configuration of the states of the separate molecules which will give a resultant thermodynamic state in the gas. Thus the negative logarithm of the chance that the separate molecules will find themselves in such a configuration of states as to give a certain thermodynamic state in the gas is the quantity H. From the relation between H and entropy one can then write that, since $-\log W_{therm.} = H$, therefore $S = R/N_A \log W_{therm.}$ Here $W_{therm.}$ signifies the thermodynamic probability.

33. Maxwell's Deduction of the Distribution of Velocities.— The law which was deduced by Boltzmann from a study of the equilibrium state existing among the molecules making elastic

impacts was originally deduced by Maxwell from considerations of pure probabilities. It happens that the assumptions which must be made concerning the behavior of the molecules fall into a general set of conditions in the theory of probabilities which at once specify the form of the distribution law.* These conditions are so general that no specific applications to molecules need be made, only the molecules must be assumed to fulfil certain conditions. These conditions imply that a steady state has been reached and no remnants of external disturbances exist in the gas. It also requires that enough molecules be considered so that deviations from a mean condition throughout the gas are highly improbable. What really should be shown and must exist, as the conditions give the true distribution law, is that the equilibrium resulting from elastic impacts fulfils the conditions imposed in the derivation.

Let the gas molecules be assumed to obey the following conditions.

1. Assume equilibrium with enough molecules so that the number of molecules in any region is the same and so that the velocities in any direction are equal. In other words, assume that the numbers considered are great enough so that in any volume of the gas there will be equal numbers of molecules and that the molecules will have the same velocities in all directions. The assumption also demands that no clumping or aggregation of the molecules exists and that all convection or mass movements in the gas be absent. These assumptions lead to the following consequences:

a. The components of velocity along any system of coordinates are equal.

b. This isotropy of the gas makes it immaterial what coordinate system the results are expressed in. In other words, an equating of the functions expressed in different coordinate systems would amount to a statement of the isotropy of the gas.

* Maxwell's original proof is, however, not a definite proof of the conditions existing among the molecules as pointed out by Boltzmann. "On the one hand, the distribution of velocities in a stationary state is called forth by impacts. On the other hand, in the deduction which follows the existence of impacts does not enter in at any point, for no use is made of the laws of impact. This proof then, if it be assumed correct, could be used to show that Maxwell's law holds if no impacts took place, a thing which is impossible. A rigorous proof of the law can then only come from a study of the impacts."

2. The velocities along any three coordinate axes are independent of each other. A statement of this independence would be included in multiplying the chance of a velocity along any one axis, which depends on the velocity only, with the chance of the velocity along one of the other axes and stating that the resultant chance is the chance of a combined velocity containing the two components, for the multiplication of two probabilities to give the resultant probability can only occur if the probabilities are independent phenomena.*

3. Assume the freedom of velocity distribution from any other influences, that is, assume that the chance of the velocity of a molecule lying between certain limits is a function of the *velocity considered and of the limits only.* This is the same as asserting that the distribution of molecular velocities can be represented by a probability function and is similar to the assumption made in deducing the distribution of the free paths.

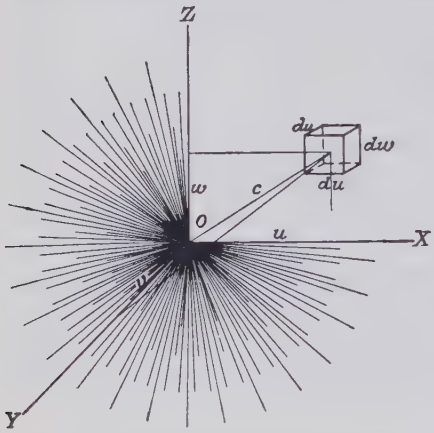

FIG. 18.

Having laid down the assumptions concerned, it is next convenient to visualize the molecular velocities in the following manner:

Assume that at a given instant all the velocities of the molecules in a volume of gas could be photographed as vectors whose lengths give the magnitude and whose directions are the directions of all the molecular motions at that time. These vectors could then be arranged so that they all started from a common origin O. If this were done, the resulting figure in space would resemble a perfectly symmetrical spiny sea urchin radiating from the center O. Such a figure is represented in Fig. 18. The

*This assumption is not at once obvious, for actually among the molecules the components of velocity along any three coordinate axes u, v, and w are subject to certain relations, to wit, the conservation of momenta and of energy in the case of real molecules. It, however, happens that the laws of impact so affect the relations that the conditions are fulfilled and the deduction accordingly leads to the correct result.

spines would have varying lengths, there being a few very long ones and a few short ones, with the length of most of them lying about a certain mean value. If about O the two spheres be drawn of radii c and $c + dc$, the vectors ending between these two would constitute all the velocities present that had values lying between c and $c + dc$.

Now let O be chosen as the origin of any rectangular system of coordinates x, y, z. Then any given velocity vector c could be decomposed into components u, v, and w along x, y, and z. Thus the relation $c^2 = u^2 + v^2 + w^2$ may be assumed to apply between the components and c.

From assumption 3 it can be stated that the chance that an x velocity component ends between u and $u + du$ is purely a function of the values of u and du, *i.e.*, it may be written $f(u)du$. Since the velocities are similar and equivalent (assumption 1*a*) in all directions, the chance of a velocity component along y having values between v and $v + dv$ and one along z of having values between w and $w + dw$ is expressed as $f(v)dv$ and $f(w)dw$ respectively. The chance that a velocity vector ends simultaneously between u and $u + du$, v and $v + dv$, and w and $w + dw$ is, from assumption 2, given by the product

$$f(u)f(v)f(w)dudvdw.$$

This same group of coordinates goes to make up a single vector c as stated above. The chance that this single velocity of value c ends in the volume element $dudvdw$ is then, by assumption 3, a function of c and of $dudvdw$ only. That chance may be expressed as $F(c)dudvdw$, following the notation above. For convenience, it may just as well be written as $\phi(c^2)\ dudvdw$, where ϕ represents the appropriate form of the function. It now becomes possible to express the independence of coordinate systems assumed in 1*b* in the form

$$f(u)f(v)f(w)dudvdw = \phi(c^2)dudvdw,$$

or

$$f(u)f(v)f(w) = \phi(u^2 + v^2 + w^2).$$

This condition at once determines the form of the distribution law, for it equates the product of a set of functions to a function of the sum of the variables. Such a relation is indicative of a logarithmic relationship between the variables. Maxwell goes at once to the law from the implication contained in this. It is, however, possible to deduce this relation mathematically from the above equation.

For the particular value of c chosen, $\phi(c^2)$ is a constant, that is, the differential of this quantity is equal to 0, hence $d[\phi(c^2)] = 0 = d[f(u)f(v)f(w)]$. Differentiating,

$$f'(u)f(v)f(w)du + f(u)\,f'(v)f(w)dv + f'(w)f(u)f(v)dw = 0,$$

where the symbol $f'(u)$ represents the derivative of $f(u)$, etc. Dividing by $f(u)\,f(v)\,f(w)$ the equation becomes

$$\frac{f'(u)}{f(u)}\,du + \frac{f'(v)}{f(v)}\,dv + \frac{f'(w)}{f(w)}\,dw = 0.$$

Now $c^2 = u^2 + v^2 + w^2$, hence as c is a constant $udu + vdv + wdw = 0$. Multiplying this by a constant λ and adding the resultant to the equation for the ratio of the derivative of the function to the functions

$$\left(\frac{f'(u)}{f(u)} + \lambda u\right)du + \left(\frac{f'(v)}{f(v)} + \lambda v\right)dv + \left(\frac{f'(w)}{f(w)} + \lambda w\right)dw = 0$$

is obtained.

Since by assumption 2 the velocity components are independent of each other this equation can be 0 only if each one of the terms separately is equal to 0. This can be expressed by the equations below:

$$\frac{f'(u)}{f(u)}\,du = -\lambda u du, \text{ or } \log f(u) = -\frac{\lambda}{2}\,u^2 + \log A.$$

$$\frac{f'(v)}{f(v)}\,dv = -\lambda v dv, \text{ or } \log f(v) = -\frac{\lambda}{2}\,v^2 + \log A.$$

$$\frac{f'(w)}{f(w)}\,dw = -\lambda w dw, \text{ or } \log f(w) = -\frac{\lambda}{2}\,w^2 + \log A.$$

Here A is a constant of integration to be determined later. From these equations it follows that

$$f(u) = Ae^{-\frac{\lambda}{2}u^2}.$$

$$f(v) = Ae^{-\frac{\lambda}{2}v^2}.$$

$$f(w) = Ae^{-\frac{\lambda}{2}w^2}$$

Call $\dfrac{\lambda}{2} = \dfrac{1}{\alpha^2}$.

Thus $f(u)du$, the chance that a molecule has the velocity between u and $u + du$, is given by

$$f(u)du = Ae^{-\frac{u^2}{\alpha^2}}\,du.$$

If there are N molecules present in a cm^3 the number having velocities of this value is given by

$$N_{du} = NAe^{-\frac{u^2}{\alpha^2}} du \text{ and likewise for } v \text{ and } w.$$

$$N_{dv} = NAe^{-\frac{v^2}{\alpha^2}} dv.$$

$$N_{dw} = NAe^{-\frac{w^2}{\alpha^2}} dw.$$

This is the same equation as was obtained in Boltzmann's deduction above.

34. Evaluation of Constants A, and α of Boltzmann and Maxwell's Deductions.—It now remains to determine the constants A and α. This is done as follows:

$$N = \int_{-\infty}^{+\infty} N_{du},$$

hence

$$N = AN \int_{-\infty}^{+\infty} e^{-\frac{u^2}{\alpha^2}} du.$$

This is a definite integral whose value is $\frac{2}{2\frac{1}{\alpha}}\sqrt{\pi}$.

Therefore

$$1 = A\alpha\sqrt{\pi}$$

or

$$A = \frac{1}{\alpha\sqrt{\pi}}.$$

Thus

$$N_{du} = N\frac{1}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du$$

$$N_{dv} = N\frac{1}{\alpha\sqrt{\pi}} e^{-\frac{v^2}{\alpha^2}} dv$$

$$N_{dw} = N\frac{1}{\alpha\sqrt{\pi}} e^{-\frac{w^2}{\alpha^2}} dw$$

and

$$f(u) = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}}.$$

$$f(v) = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{v^2}{\alpha^2}}.$$

$$f(w) = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{w^2}{\alpha^2}}.$$

The chance of a velocity ending simultaneously between u and $u + du$, v and $v + dv$, and w and $w + dw$ is then

$$f(u)f(v)f(w)dudvdw = \frac{1}{\alpha^3\pi^{\frac{3}{2}}} e^{-\frac{u^2+v^2+w^2}{\alpha^2}} dudvdw.$$

$c^2 = u^2 + v^2 + w^2$, and $dudvdw$ is given by $dc \times cd\theta \times c \sin \theta d\phi$ in Fig. 19. Hence

$$f(u)f(v)f(w)dudvdw = \frac{1}{\alpha^3 \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}} c^2 dc \sin \theta d\theta d\phi.$$

This is the chance of the velocity ending in the element of volume $dudvdw$, or between c and $c + dc$, θ and $\theta + d\theta$, and ϕ and $\phi + d\phi$. To get the chance of a velocity ending between c and $c + dc$ this must be integrated for all values of θ from 0 to π and for ϕ from 0 to 2π, that is, it must be integrated all over the spherical shell of thickness dc lying between c and $c + dc$. If there are N molecules present in a cm^3, the number having velocities between c and $c + dc$ is obtained by multiplying the quantity

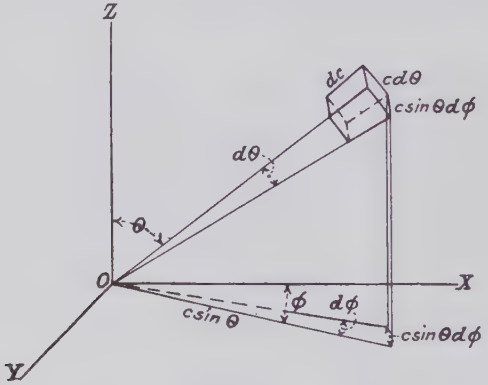

Fig. 19.

above by N and integrating over the limits mentioned. Hence

$$N_{dc} = \frac{N}{\alpha^3 \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}} c^2 dc \int_0^{\pi} \int_0^{2\pi} \sin \theta d\theta d\phi$$

$$= \frac{4N}{\alpha^3 \sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc.$$

This same operation can be carried out more simply by writing

$$f(u)f(v)f(w) = \frac{1}{\pi^{3/2}\alpha^3} e^{-\frac{c^2}{\alpha^2}}.$$

The chance that this vector ends between c and $c + dc$ is then $f(u)f(v)f(w)$ times the volume between c and $c + dc$ in the spherical shell. This has a surface $4\pi c^2$ and is dc thick, and hence the chance of ending in dc is given by

$$P_{dc} = f(u)f(v)f(w)4\pi c^2 dc$$

$$= \frac{4}{\alpha^3 \sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc.$$

If there are N molecules present in a cm^3 the number of vectors ending between c and $c + dc$ is

$$N_{dc} = \frac{4N}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc.$$

The meaning of α may now be determined by considering the form of this function. Unlike the distribution of free paths, it is found that, at $c = 0$, $N_{dc} = 0$, and at $c = \infty$, $N_{dc} = 0$. In between the function is always positive, and hence it has a maximum. This maximum represents the speed for which N_{dc} is the greatest; that is to say, it is the *most probable speed.* To find this N_{dc} must be differentiated and equated to 0.

$$\frac{dN_{dc}}{dc} = 0 = -\frac{2c}{\alpha^2} e^{-\frac{c^2}{\alpha^2}} c^2 dc + e^{-\frac{c^2}{\alpha^2}} 2c dc,$$

whence

$$c = \alpha.$$

Hence the α of this equation represents *the most probable speed.*

35. Plot of the Law and Various Averages.—It is now possible to plot the curve representing this law. For the purpose of plotting it is to be noted that the equation may be written in terms of the parameter $\frac{c}{\alpha}$, that is, the velocities may be expressed in terms of their values relative to α, the most probable speed, *i.e.*, relative to the maximum of the curve. Then to plot it one may write

$$N_{dc} = \frac{4}{\sqrt{\pi}} N \frac{c^2}{\alpha^2} e^{-\frac{c^2}{\alpha^2}} \frac{dc}{\alpha} = \frac{4N}{\sqrt{\pi}} x^2 e^{-x^2} dx, \text{ where } x = \frac{c}{\alpha}.$$

If, then, a suitable value for dx be chosen, say $dx = dc/\alpha = 0.10$, N_{dc} may be evaluated for various values of x. Such a plot is shown in Fig. 20, where N was chosen as 100.

It is seen at once that the curve is not symmetrical as regards $c = \alpha$, or $x = 1$. In fact, a slightly greater area lies to the right of $x = 1$. It is then obvious that α will not represent the average speed but will be less. Let the average speed $\bar{c}$ be computed

$$\bar{c} = \int_0^\infty \frac{cN_{dc}}{N} = \frac{1}{N} \int_0^\infty \frac{4N}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^3 dc.$$

Putting it into terms of $c/\alpha = x$, $dc/\alpha = dx$,

$$\bar{c} = \frac{4\alpha}{\sqrt{\pi}} \int_0^\infty x^3 e^{-x^2} dx.$$

This, again, is a definite integral whose value leads to $\bar{c} = 2\alpha/\sqrt{\pi}$. Thus the average speed is $2/\sqrt{\pi}$ times the most probable speed, that is, $\bar{c} = 1.128\alpha$.

Finally, the dissymmetry of the curve demands the use of a third average velocity. The molecular velocities are found experimentally from the relation that

$$p = \frac{1}{3}nm\bar{c}^2, \text{ where } nm = \rho, \text{ hence } \sqrt{\bar{c}^2} = \sqrt{\frac{3p}{\rho}}.$$

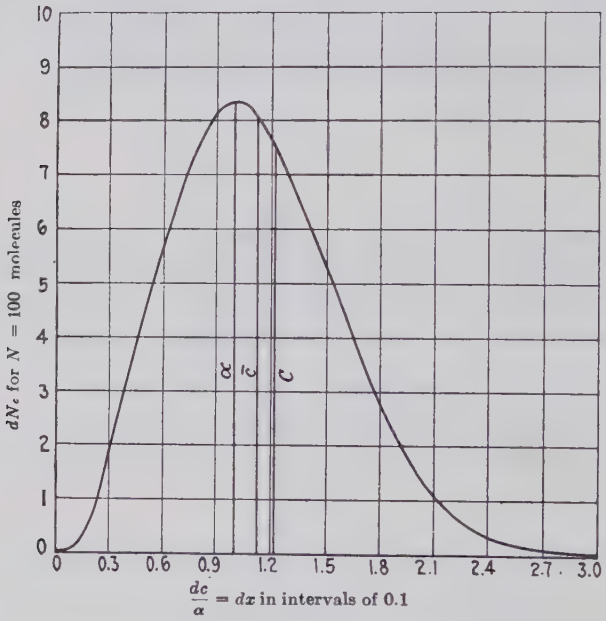

FIG. 20.

Thus the actual values of the velocities obtained *are not the average velocities* but the *square root of the average squared velocities* (Sec. 11). This, owing to the dissymmetry of the curve, will again be towards higher values of the velocity than either the most probable speed or the average speed, since in such an average the higher velocities will receive greater prominence. The root-mean-square speed, $\sqrt{\bar{c}^2}$, hereafter to be designated by C, is found as follows

$$C = \sqrt{\int_0^\infty \frac{c^2 N_{dc}}{N}} = \sqrt{\left[\frac{4}{\alpha^3\sqrt{\pi}}\int_0^\infty c^4 e^{-\frac{c^2}{\alpha^2}} dc\right]}.$$

Putting $x = c/\alpha$,

$$C = \sqrt{\left[\frac{4\alpha^2}{\sqrt{\tau}}\int_0^\infty x^4 e^{-x^2}\,dx\right]} \text{ is obtained, whence}$$

$$C = \sqrt{\left[\frac{3\alpha^2}{2}\right]} = \sqrt{\frac{3}{2}}\,\alpha = 1.224\alpha.$$

Thus one has to remember that molecular speeds are designated in terms of three quantities—the most probable, the average, and the square root of the mean square speed—which are related to each other by the equation

$$\alpha : \bar{c} : C = 1 : \frac{2}{\sqrt{\tau}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.224.$$

The ratio of $\bar{c}$ to C is seen to be $\sqrt{\frac{8}{3\tau}}$, or 0.922. Owing to these differences great care must be used in applying the equations of the kinetic theory in order to insure the use of the proper average.

36. Maxwell's Distribution Law and the Theorem of Equipartition.—In Section (9) of Chapter II it was shown that if one assumed the kinetic interpretation of gaseous pressure, and the experimental justification of Avogadro's rule, one was led to the conclusion that the average translational kinetic energy of each gas in a mixture of gases in equilibrium was the same. This conclusion was there asserted to be one manifestation of a more general law known as the Maxwell-Boltzmann law of equipartition of energy. It was also stated in a foot note that the deduction of the pressure of a gas on the basis of simple kinetic theory assumptions in Section (5) contained another aspect of the same assumption in the postulate that the velocity of the gas molecules along any one of the sides of the rectangular box was the same.

Inasmuch as the purpose of the kinetic theory is to formulate mathematically the behavior of gases on the basis of Newtonian mechanics it would seem more fitting that the law of equipartition should be deduced as a consequence of the assumptions of the fundamental kinetic theory by logical mathematical processes, and then be used in predicting Avogadro's rule, rather than the reverse. It happens that the first rigorous attempts at such a deduction resulted from some of the analyses made in the process of the deduction of Maxwell's law of distribution of velocities by the Boltzmann method. Furthermore the Maxwell deduction of this law also contained the tacit assumptions of the law of

equipartition restricted to translational velocities in its fundamental postulates. Finally the application of the law of equipartition to the interpretation of many physical problems is made by the use of the distribution law in such a form that it expresses the law of equipartition of energy. Accordingly since the law of equipartition of energy is bound up so intimately with the law of distribution of velocities it seems fitting that a brief discussion of its derivation should occur at this point. The application of the theorem of equipartition to the study of specific heats and the limitations of the theorem may, however, be properly discussed in a later chapter.

Before proceeding with the discussion it may be well to point out that very few questions in the kinetic theory of gases have been the subject of so much controversy as the questions of the validity of the various attempted proofs of the theorem of equipartition. While in the earlier years the problem was treated from the point of view of elastic molecular impacts, it has in recent years been studied almost exclusively by the more general and powerful methods of statistical mechanics. Unfortunately, the study of this subject would furnish the material for a book in itself, and so cannot be discussed at this point. From the more elementary point of view a very good idea of the problem can be obtained from both the elastic-solid-impact analysis[35] and from the elementary analysis by means of statistical mechanics given in Clemens-Schaefer's "Einführung in die Theoretische Physik," vol. 2, part I, pages 401–403, and Chap. X, page 418 and especially pages 450 and 458ff. This[20] does not contain a critical review of the subject. For this reference may be made to Jeans "Dynamical Theory of Gases," Chaps. III, IV, and V.[21] There is also a very exhaustive study of the problems of statistical mechanics in an article by P. and T. Ehrenfest[22] in "Encyclopédie des Sciences Mathématiques," vol. IV, I, Paris, 1915, which contains further references to later literature and a comment by Borel.

Historically, the theorem of equipartition of energy of molecules in a system of varying masses was first enunciated by Waterston[23] in 1845. His proof, according to a footnote by Rayleigh, could hardly be accepted as valid, although at the time Rayleigh commented on the importance of the contribution. Maxwell,[24] in 1859, independently arrived at the same conclusions. In 1861, Boltzmann[25] again brought the question into prominence and

extended it to all degrees of freedom in equilibrium. The matter was again discussed by Maxwell in a paper in 1879. Since then the question has been variously attacked by many workers, including Lorentz, Gibbs,[22] Jeans, and others chiefly in the field of statistical mechanics. Jeans[21] in particular believed to have derived the theorem in a rigorous fashion. Other workers appear to be dissatisfied with his deduction, and at present it is difficult to judge the exact status of the question. The question hinges largely on the implications included in the postulates on the basis of which the particular deduction is made. The exact situation might be stated as follows: Mathematical proofs of the theorem of equipartition have been given which very nearly, if not completely, establish the theorem as a result of the underlying assumptions of the application of Newtonian mechanics to gases made up of moving particles as postulated by the kinetic theory. On the other hand, while the experimental evidence to some extent bore out the predictions of the theorem, it seemed to fall seriously short in many cases. The explanation of this failure of the equipartition theorem was interpreted in the light of the new quantum effects.[27] The significance of these effects seems to lie in a direction which points towards a failure of the Newtonian mechanics and the laws of electrodynamics under certain conditions. If this explanation is correct, the failure of the equipartition theorem may in some measure be led back to a failure of the molecules to obey the laws of Newtonian mechanics assumed in the deduction of the equipartition theorem. This type of departure from classical mechanics is to be seen in the case of the behavior of C_p[28] for H_2 at low pressures and is not related to the relativity modifications. The application of the quantum mechanics to these phenomena then, in reality, is not a modification but rather an extension of the theorem to cover the problems introduced by non-Newtonian mechanics in the sense above mentioned. Thus it may be asserted that to a limited extent experiment bears out the predictions of the theorem of equipartition, while it shows clearly that the underlying assumptions are not completely adequate to describe all phenomena. The result is that it at present seems futile to discuss much further the question of the adequacy of the proofs of the theorem when it is faced with the difficulties encountered in the quantum effects. Considering the evidence as a whole, it would be not far from correct to accept the theorem as proved for practi-

cal purposes to the extent that the observed quantum effects will permit it.

In what follows a brief deduction of the law of equipartition as applied to translational motions of the molecules will be given in a manner similar to that used by Boltzmann following from his proof of the distribution law.[35] The treatment here given is taken from Clemens-Schaefer and is a direct consequence of one of the steps of the deduction of the distribution law as given in Sec. 31. Following the derivation, a brief discussion of this type of derivation will be given as laid down by Jeans.[21] Finally, the distribution law for translational velocities will be written in a form which includes the assumption of equipartition of energy. The law will then be written in other forms as deduced by Clemens-Schaefer from statistical mechanics for the case of rotational energies and for the case where the energies in equilibrium may be in any form. The equipartition law written in these forms, even though not deduced, will be of service in later applications of the theorem of equipartition and distribution of energies among the molecules.

Deduction of the Law of Equipartition for Translational Energies in Gaseous Mixtures.—All quantities referring to one of the gases of a binary gaseous mixture may be designated by the subscript 1, and all those of the other gas by the subscript 2. Then it is possible to consider impacts of molecules of one of the gases with each other, impacts of the molecules of the other gas with each other, and impacts of molecules of the one gas with molecules of the other gas. Now in Sec. 31, in the Boltzmann deduction of the distribution law, it was shown that the distribution law is defined by the relation expressing equilibrium in the form:

$$\bar{F}\,\bar{F}' - FF' = 0.$$

This relation also contains a proof of the law of equipartition for the translational energies in a gas, as will be seen in what follows. The expression above may at once be carried over to the case for equilibrium in a gaseous mixture if the proper subscripts are added to the letters. Before writing these expressions, the above expression may be reduced to the form independent of the number of the molecules present by dividing by the number of molecules per cm^3, or N. This gives the expression in the form

$$\bar{f}f' - ff' = 0.$$

Applying it now to the mixtures of the two gases, three equations are obtained applying in turn to gas 1, gas 2, and to the mixture of the gases.

$$\bar{f}_1\bar{f}_1' - f_1f_1' = 0 \text{ gas 1.}$$
$$\bar{f}_2\bar{f}_2' - f_2f_2' = 0 \text{ gas 2.}$$
$$\bar{f}_2\bar{f}_1' - f_2f_1' = 0 \text{ gas 1 and gas 2.}$$

As in Sec. 32, the first two expressions lead to the distribution law with the proper subscripts added to the constant terms. These take the form

$$f_1 = A_1{}^3 e^{-\frac{1}{\alpha_1{}^2}(u^2+v^2+w^2)} \text{ and } f_2 = A_2{}^3 e^{-\frac{1}{\alpha_2{}^2}(u^2+v^2+w^2)},$$

where $A_1 = \dfrac{1}{\alpha_1\sqrt{\pi}}$ and $A_2 = \dfrac{1}{\alpha_2\sqrt{\pi}}$.

Accordingly,

$$f_1 = \frac{1}{\alpha_1{}^3\pi^{3/2}} e^{-\frac{u^2+v^2+w^2}{\alpha_1{}^2}} \text{ and } \qquad f_2 = \frac{1}{\alpha_2^3\pi^{3/2}} e^{-\frac{u^2+v^2+w^2}{\alpha_2{}^2}}$$

which may also be directly related to the average squared velocities $C_1{}^2$ and $C_2{}^2$ by the relations found in Sec. 35. The third relation between the dashed and undashed letters and the accented and unaccented letters will then be expressions of the form above, in which the velocity vectors u, v, and w take on the designation appropriate to their type. Simple algebraic manipulations of these expressions lead to an expression between the $1/\alpha_1$ and $1/\alpha_2$, which, translated in terms of the averaged square velocities, give the simple relation

$$\frac{1}{2}m_1C_1{}^2 = \frac{1}{2}m_2C_2{}^2.$$

This is the same expression deduced from Avogadro's rule and the pressure relation in a gas in Sec. 9 and which states equipartition. Thus the theorem of equipartition has been proved for translational motion for the case of a gas, using the assumptions of elastic impacts only. The validity of such a proof lies only in the question as to whether the conditions implying equipartition were not contained in one of the postulates underlying the theory. This was, in fact, done in deducing the law of distribution of velocities in Maxwell's fashion, through the assumption of independence of velocity coordinates coupled with the other assumptions. The proof of equipartition in the Boltzmann treatment above is as correct as the assumptions underlying the derivation of the distribution law. According to Jeans,[21] the derivation of

Boltzmann is not much better off in regard to the implied assumptions than Maxwell's original distribution-law derivation was. In Boltzmann's case the proof included the assumption of independence of space and velocity coordinates instead of the independence of velocity components among themselves. The question of the distribution law has been discussed by Boltzmann[29] and by Lorentz.[30] Burbury[21] questions the validity of this proof, but the doubt is not shared by Jeans. In any case, the proof here given is not necessarily very rigorous, and as it is specialized in its scope, recourse should, in general, best be had to the more complete proofs in statistical mechanics.

It is of use to consider certain modifications of the distribution law which express at the same time the law of equipartition of energy. These laws are deduced from statistical reasoning and will only be given here in brief. The Maxwell distribution law in the form given in Sec. 35, expressing equipartition for translational energies, may be transformed into a form frequently written and indicating an energy distribution rather than a velocity distribution. The equation given in Sec. 35 was

$$N_{dc} = \frac{4N}{\alpha^3 \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}} c^2 dc.$$

The c^2 and α^2 may be multiplied by m, the mass of a molecule, and the c^3 and α^3 by $m^{3/2}$. The equation then becomes

$$N_{dc} = \frac{4Nm^{3/2}}{m^{3/2}\alpha^3 \pi^{3/2}} c^2 e^{-\frac{mc^2/2}{m\alpha^2/2}} dc.$$

Now it was shown in Sec. 5 that $\frac{1}{3}NmC^2 = RT$, and in Sec. 35 that $\alpha^2 = \frac{2}{3}C^2$, whence $\frac{1}{2}Nm\alpha^2 = RT$. If the gas constant, R per cm^3, divided by N, the number of molecules per cm^3, be called k, where k is the average energy taken to raise the temperature of one molecule 1°C., then it is at once found that $\frac{1}{2}m\alpha^2 = kT$. But $\frac{1}{2}m\alpha^2$ is the most probable kinetic energy of the molecules. Thus $\frac{1}{2}m\alpha^2$ can be expressed in terms of temperature from the relation above. The constant k is called the Boltzmann constant. Putting this into the equation above the relation is had in the form

$$N_{dc} = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}} dc.$$

Occasionally, it is found convenient to write the expression above in another form. Designating $\frac{1}{2kT}$ by the letter h, the equation becomes

$$N_{dc} = 4\pi N\left(\frac{hm}{\pi}\right)^{3/2} c^2 e^{-hmc^2} dc,$$

which is a form often used in the literature.

For the case of rotational equipartition the distribution of rotational energies is given by

$$N_{d\omega} = 4\pi N\left(\frac{I}{2\pi kT}\right)^{3/2} \omega^2 e^{-\frac{I\omega^2}{2kT}} d\omega,$$

where $N_{d\omega}$ is the number of molecules out of N that have angular velocities between ω and $\omega + d\omega$, and I is the moment of inertia.

Extension of the Distribution Law to Include Potential Energy.— It is of importance to consider the extension of the distribution law to the case of molecules which find themselves in a field of force. This situation is frequently encountered in the problems of molecules exerting attractive forces on each other, in the case of molecules passing through the force field at the boundary of a liquid or a solid, and of molecules which find themselves in a gravitational field. To consider the case of molecules of a gas in equilibrium in a force field, one can choose the case of the earth's gravitational field for convenience. To this end an infinitely long vertical cylinder filled with gas in the earth's gravitational field may be considered. This cylinder must be assumed to be isolated from all external disturbances and to have been left to itself long enough to have gained equilibrium; that is, to have reached a condition where all net mass, momentum, or heat transfer has ceased. Under these conditions one must first consider what the temperature conditions in the cylinder are. The reason for this lies in the fact that if one regard a molecule at some point h above the base of the cylinder, the molecule under the force of gravity will have work done on it of value mgh in going to the bottom layer, where m is the mass of the molecule and g is the gravitational acceleration. This decrease in potential energy leads to an increase in the velocity u of the molecule, and hence for every molecule going downward to $h = 0$ it leads to an increase in the average velocity and thus the temperature of the gas. On the other hand, every

molecule going upward from 0 to h will lose an amount of kinetic energy or heat in order to gain its higher position in the potential field. Thus molecules going to h have their kinetic energy reduced, while molecules descending increase that energy in the region to which they go. Thus it might seem at first sight as if α, the most probable velocity at h, might be less than α_0, the similar velocity at $h = 0$, and thus that the temperature T_0 at $h = 0$ might be greater than the temperature at h. Measurements, however, show the temperature to be the same throughout the cylinder. The explanation of this apparent paradox was accomplished by Boltzmann as follows. Under *equilibrium* conditions at any point such as h, one may assume the Maxwellian distribution of velocities to exist with a most probable velocity α and a corresponding temperature T with N molecules per cm^3. At $h = 0$ one can assume a probable velocity α_0, a temperature T_0 and N_0 molecules per cm^3. The number of molecules at h and 0, respectively, with velocities between c and $c + dc$ will then be given by

$$dN_c = \frac{4N}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc,$$

$$dN_{c_0} = \frac{4N_0}{\alpha_0{}^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha_0{}^2}}dc.$$

Consider a horizontal plane P between 0 and h and fix attention on the movement of molecules across unit area of P per second in both directions. To do this if h be made of the order of a free path, one need only regard u, the vertical component of velocities of the molecules going down from h, and up from $h = 0$. The number of molecules per second going downward through unit area of P from h will be u times the $\frac{N}{\alpha\sqrt{\pi}}e^{-\frac{u^2}{\alpha^2}}du$ molecules of velocity between u and $u + du$ in unit volume at h. Of those molecules going toward P from above, all will pass through as the earth's field is acting to *aid* their passage downward. The total number of molecules of all velocities u along the x-axis passing downward through 1 cm^2 of P per second will then be

$$\frac{N}{\alpha\sqrt{\pi}}\int_0^\infty ue^{-\frac{u^2}{\alpha^2}}du = \frac{N\alpha}{2\sqrt{\pi}}.$$

For the molecules of velocity u the number headed upward from $h = 0$ which would strike unit area of P per second is

$$\frac{N_0}{\alpha_0\sqrt{\pi}} u e^{-\frac{u^2}{\alpha_0^2}} du.$$

Of these, however, only those whose velocity u is such that $(u \geq \sqrt{2gh})$ or $\frac{1}{2}mu^2 \geq mgh$ will succeed in traversing the distance h from $h = 0$ to h against the earth's gravitational field. Hence the number of molecules of all velocities along x from $h = 0$ which pass through unit area of P per second and reach h is

$$\frac{N_0}{\alpha_0\sqrt{\pi}} \int_{\sqrt{2gh}}^{\infty} u e^{-\frac{u^2}{\alpha_0^2}} du = \frac{N_0\alpha_0}{2\sqrt{\pi}} e^{-\frac{2gh}{\alpha_0^2}}.$$

Now absence of net mass motion, *i.e.*, equilibrium, says that the number of molecules of all velocities involved in the exchange across P between $h = 0$ and h must be equal. Hence one can write that $N\alpha = N_0\alpha_0 e^{-\frac{2gh}{\alpha_0^2}}$.

If one next consider the transfer of kinetic energy of translation across P, one need only remember that each molecule of velocity component along u starts to carry with itself an energy $\frac{1}{2}mu^2$ in either direction. Hence the total energy transfer downward from h across unit area of P per second is

$$\frac{N}{\alpha\sqrt{\pi}} \frac{m}{2} \int_0^{\infty} u^3 e^{-\frac{u^2}{\alpha^2}} du = \frac{Nm\alpha^3}{4\sqrt{\pi}}.$$

The molecules moving upward from $h = 0$ to h will each only succeed in carrying an energy $\frac{1}{2}mu^2 - mgh$ to the layer at h so that the transfer of energy upward from $h = 0$ to h through unit area of P per second for molecules of all velocities u will be

$$\frac{N_0}{\alpha_0\sqrt{\pi}} \int_{\sqrt{2gh}}^{\infty} \left(\frac{1}{2}mu^2 - mgh\right) u e^{-\frac{u^2}{\alpha_0^2}} du = \frac{N_0\alpha_0^3}{2\sqrt{\pi}} \frac{m}{2} e^{-\frac{2gh}{\alpha_0^2}}.$$

Here again absence of a net energy transport corresponding to equilibrium demands that

$$N\alpha^3 = N_0\alpha_0{}^3 e^{-\frac{2gh}{\alpha_0{}^2}}.$$

But the absence of net mass transport also set the condition that

$$N\alpha = N_0\alpha_0 e^{-\frac{2gh}{\alpha_0{}^2}}.$$

Since both these conditions obtain for equilibrium, it is clear that they can simultaneously hold true only if $\alpha^2 = \alpha_0{}^2$. This means that the most probable velocity α at h must be equal to α_0, the most probable velocity at $h = 0$, which, by multiplying both sides of the equation by the same appropriate constants, yields the equality of temperature throughout the cylinder. It is therefore clear that the discussion which appeared to lead to an inequality of temperature was incomplete and incorrect. The source of the error in the reasoning lay in another item exhibited by the equations above. Since

$$N\alpha = N_0\alpha_0 e^{-\frac{2gh}{\alpha_0{}^2}},$$

and since $\alpha = \alpha_0$, therefore $N = N_0 e^{-\frac{2gh}{\alpha^2}}$. This says that the number of molecules per unit volume N at h is less than the number N_0 of molecules per unit volume at $h = 0$ by the factor $e^{-\frac{2gh}{\alpha^2}}$. Thus while the downward-moving molecules all get through and deliver more energy to the lower layers, there are just enough more molecules, due to the concentration change, of an energy which diminished by mgh will reach h with the energy taken out by the downward-moving molecules to maintain equilibrium.

If one regard the expression $N = N_0 e^{-\frac{2gh}{\alpha^2}}$ and multiply numerator and denominator of the exponent with $m/2$, one has at once that

$$N = N_0 e^{-\frac{mgh}{\frac{m}{2}\alpha^2}} = N_0 e^{-\frac{mgh}{kT}},$$

where $kT = \frac{m\alpha^2}{2}$, α being the most probable velocity common to all portions of the gas. It is seen therefore that if one regard the concentration of the molecules in the cylinder, it varies exponentially from $h = 0$ on upward and does so the more

rapidly the greater the mass of the molecules m and the greater the acceleration due to the force field. If both sides of the equation be multiplied by $\frac{1}{3}mC^2$ one has

$$\frac{1}{3}NmC^2 = \frac{1}{3}N_0mC^2e^{-\frac{mgh}{kT}},$$

or

$$p = p_0e^{-\frac{mgh}{kT}},$$

which is the well-known law of atmospheres.

If one fixes one's attention on the N molecules at a height h above the origin, it is clear that the number of molecules of velocity between c and $c + dc$ will be given by

$$\frac{4N}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc.$$

Replacing N by its equivalent $N = N_0e^{-\frac{2gh}{\alpha^2}}$, one has

$$N_{dc} = \frac{4N_0}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2+2gh}{\alpha^2}}dc.$$

It is seen that the number of molecules of velocities between c and $c + dc$ at a height h in a potential field for which the potential gh is given by $gh = \chi$ is $N_{dc\chi} = \frac{4N_0}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2+2\chi}{\alpha^2}}dc$. Setting $\frac{mc^2}{2} = E_k$, $\frac{m}{2}\alpha^2 = kT$, and $mgh = E_p$, where E_k and E_p are the kinetic and potential energies, respectively, one can write the law above by the appropriate multiplication with $m/2$ or powers thereof as

$$dN_E = \frac{2N_0\sqrt{E_k}}{\pi^{\frac{1}{2}}(kT)^{\frac{3}{2}}}e^{-\frac{E_k+E_p}{kT}}dE.$$

This is a more general form of the law of distribution of energies including kinetic energy of translation and the potential energy.

From the relation $N = N_0e^{-\frac{mgh}{kT}}$ deduced above, one may generalize the expression to apply to any force field. If h apply to a distance x along the x-axis, and if gh be represented by the potential χ, then mgh in the more general sense becomes

$m\int_0^x \frac{\partial \chi}{\partial x}dx$. For a distribution of potential along y the corresponding quantity at y is $m\int_0^y \frac{\partial \chi}{\partial y}dy$ and at z it is $m\int_0^z \frac{\partial \chi}{\partial z}dz$. If then the chance be considered that a molecule has a velocity between u and $u + du$ at a point x in a potential field, this chance will be

$$dW_u = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{1}{kT}\left(\frac{mu^2}{2} + m\int_0^x \frac{\partial \chi}{\partial x}dx\right)} du$$

and likewise for the components v and w along y and z at y and z:

$$dW_v = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{1}{kT}\left(\frac{mv^2}{2} + m\int_0^y \frac{\partial \chi}{\partial y}dy\right)} dv,$$

$$dW_w = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{1}{kT}\left(\frac{mw^2}{2} + m\int_0^z \frac{\partial \chi}{\partial z}dz\right)} dw.$$

The chance that a molecule at this point in the field has a velocity between u and $u + du$, v and $v + dv$, w and $w + dw$ becomes, if one set

$$\int_0^x \frac{\partial \chi}{\partial x}dx + \int_0^y \frac{\partial \chi}{\partial y}dy + \int_0^z \frac{\partial \chi}{\partial z}dz = \chi + \chi_0,$$

where χ_0 is a constant determined by the potential χ_0 at the origin, and $\frac{mu^2}{2} + \frac{mv^2}{2} + \frac{mw^2}{2} = \frac{mc^2}{2}$;

$$dW = \frac{1}{\alpha^3\pi^{3/2}} e^{-\frac{1}{kT}\left(\frac{mc^2}{2} + m\chi + m\chi_0\right)} dudvdw.$$

$$= C_1 e^{-\frac{1}{kT}\left(\frac{mc^2}{2} + m\chi\right)} dudvdw.$$

If N_0 is the number of molecules per cm^3 at $x = 0$, $y = 0$, $z = 0$, where $\chi = \chi_0$, then the number of molecules of velocity c per unit volume is $N_0 dW_{\chi_0} = N_0 C_1 e^{-\frac{1}{kT}\left(\frac{mc^2}{2} + m\chi_0\right)} dudvdw$. At any point x,y,z in the volume $dxdydz$ at a potential χ the number of molecules with velocities u, v, and w is

$$dZ = N_0 C_1 e^{-\frac{1}{kT}\left(\frac{mc^2}{2} + m\chi\right)} dudvdwdxdydz.$$

If now one integrate over all values of velocity components from 0 to ∞, the resulting number of molecules is the number of molecules in the element $dxdydz$ having a potential energy χ irrespective of their velocity. Thus

$$dN = \int_0^\infty \int_0^\infty \int_0^\infty N_0 C_1 e^{-\frac{1}{kT}\left(\frac{mc^2}{2}+m\chi\right)} dxdydzdudvdw$$
$$= N_0 C_2 e^{-\frac{m\chi}{kT}} dxdydz.$$

dN/N_0 is the chance dW that a molecule will find itself in a volume $dxdydz = d\tau$ at a point in the potential field where the potential is χ at a temperature T. This chance is seen to be $dW = C_2 e^{-\frac{m\chi}{kT}} d\tau$. As $m\chi$ is the potential energy U of the molecule, the chance that a molecule will find itself in a volume $d\tau$ in which it has the potential energy U at a temperature T is given by

$$dW = C_2 e^{-\frac{U}{kT}} d\tau.$$

This equation is of great importance in many problems of molecular behavior involving molecular force fields and thus finds frequent application.

37. Correction of Mean-free-path Equation of Clausius for Distribution of Velocities.—In the preceding deduction for the mean free paths (Sec. 18), the velocity u of the molecules was supposed to be the same for all the molecules. Actually, u is not the same and the derivation must be corrected for this fact. In the Clausius deduction the relative velocity of approach between two molecules was set as

$$r^2 = u^2 + v^2 - 2uv \cos \phi,$$

where ϕ was the angle between the velocities. This was reduced to $r = u\sqrt{2}\ \sqrt{1 - \cos \phi}$ on the assumption that $u = v$. As this is no longer the case, the value for $\bar{r}$, the average relative velocity which is given by

$$\bar{r} = \int_0^\pi \frac{r \sin \phi d\phi}{2},$$

becomes

$$\bar{r} = \frac{1}{2}\int_0^\pi \sqrt{u^2 + v^2 - 2uv \cos \phi} \sin \phi d\phi$$
$$= \frac{1}{6uv}\Big[(u^2 + v^2 - 2uv \cos \phi)^{3/2} \Big]_0^\pi$$
$$= \frac{1}{6uv}\Big[-(u^2 + v^2 - 2uv)^{3/2} + (u^2 + v^2 + 2uv)^{3/2} \Big]$$
$$= \frac{1}{6uv}\Big[-(u - v)^3 + (u + v)^3 \Big].$$

The value of $\bar{r}$ depends on whether $u > v$ or $v > u$, for if $u > v$, solution gives for $u > v$ a positive value for $u - v$ and hence $\bar{r} = \frac{3u^2 + v^2}{3u}$. If $v > u$, $(u - v)$ becomes negative, the signs are reversed and it is necessary to write $\bar{r} = \frac{3v^2 + u^2}{3v}$. Now in the preceding deduction of Clausius, u was equal to the average speed, or $u = \frac{2}{\sqrt{\pi}}\alpha$. $\bar{r}$, however, must be determined from the chance of a given u or v taken from the Maxwell law. This probability for v is $P_v = \frac{4}{\alpha^3\sqrt{\pi}}v^2e^{-\frac{v^2}{\alpha^2}}dv$, and for u is $P_u = \frac{4}{\alpha^3\sqrt{\pi}}u^2e^{-\frac{u^2}{\alpha^2}}du$. It is now necessary to average $\bar{r}$ for collisions between molecules of all possible velocities. Since $\bar{r}$ depends on both u and v and on their relative magnitudes, it is necessary to proceed as follows: First assume u constant and take into account the variation of v. Then $\bar{r}_u$ becomes

$$\bar{r}_u = \frac{4}{\alpha^3\sqrt{\pi}}\left[\int_0^u \frac{3u^2 + v^2}{3u}v^2e^{-\frac{v^2}{\alpha^2}}dv + \int_u^\infty \frac{3v^2 + u^2}{3v}v^2e^{-\frac{v^2}{\alpha^2}}dv\right].$$

The integration between 0 and u of the $\frac{3u^2 + v^2}{3u}$ term applies to values of $u > v$, and the integration from u to ∞ of the $\frac{3v^2 + u^2}{3v}$ term applies to values of $u < v$. The $\bar{r}_u$ is then the average r for all values of v. It must next be multiplied by the chance of a velocity u and integrated from 0 to ∞ to take account of the variations in the velocity u. The tedious integration will not be carried out here, and the reader is referred to the integration as carried out in Winkelmann's "Handbuch."[1,33] Integration yields

$$\bar{r} = \frac{2\alpha\sqrt{2}}{\sqrt{\pi}}, \text{ or } \frac{\bar{r}}{u} = \sqrt{2}.$$

Hence the relative velocity of the molecules to be used in the equation for the free paths is now $\sqrt{2}$ times the average velocity of a single molecule. In Clausius' derivation the value found was $\bar{r} = 4u/3$. Thus the Maxwellian distribution of velocities changes the value of the relative velocity from 1.33 to 1.41. The expression for the mean free path

$$L = \frac{1}{\frac{4}{3}\pi\sigma^2 N}$$

previously deduced now becomes

$$L = \frac{1}{\sqrt{2}\pi\sigma^2 N}.$$

38. The Mean Free Paths of Molecules in a Gas Composed of Molecules of Different Kinds.—When *one* gas molecule of diameter σ_1 in a gas composed of molecules of diameter σ_2 is considered the question arises as to which value of σ to use in the expression $L = 1/(\sqrt{2}\pi\sigma^2 N)$. A brief consideration of the elementary deduction will show that for this simple case the molecule of radius σ_1 will exclude in its path L the centers of all molecules σ_2 which lie closer than $\sigma_1/2 + \sigma_2/2$ from it, for a collision occurs whenever the centers approach within $\frac{\sigma_1 + \sigma_2}{2}$ of each other. Thus for this case it is only necessary to replace the σ of the equation for homogeneous molecules by a value $\sigma_a = (\sigma_1 + \sigma_2)/2$.

The above expression was, however, deduced on the assumption that all molecules of diameter σ_2 are at rest, and that only the one molecule of diameter σ_1 is in motion. If now all molecules are moving, that of diameter σ_1 may have a velocity $\bar{c}_1$ different from those of diameter σ_2, whose velocity may be called $\bar{c}_2$. This case may be reduced to the one above by considering all the σ_2 molecules at rest and the σ_1 molecule moving relatively to them with the *average* relative velocity. This was done for the case of all molecules having the *same* velocities in Sec. 19 and for the case of all molecules having the same *average* velocities, assuming Maxwell's distribution in Sec. 37 of Chap. IV. In the former case the relative velocity was $\bar{r} = 4\bar{c}/3$, and in the latter case it was $\bar{r} = \sqrt{2}\bar{c}$, where $\bar{c}$ was the average velocity. In the present instance the σ_1 molecules have an average velocity $\bar{c}_1$ and the σ_2 molecules an average velocity $\bar{c}_2$. It becomes necessary to der ve the expression for $\bar{r}$ for the case where the two velocities exist. For the case that the σ_2 molecules move at right angles to the σ_1 molecules the relative velocity will be $\sqrt{\bar{c}_1^2 + \bar{c}_2^2}$, for the relative velocity is the sum of the two velocity vectors at right angles to each other. Thus in this case

$\bar{r}/\bar{c}_1 = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_1$. In the earlier deductions where the molecules were all supposed to have the same velocity $\bar{c}$, $\bar{r}/\bar{c} = 4/3$, and where Maxwell's distribution was assumed, the molecules having the same average velocity $\bar{c}$, the ratio was $\bar{r}/\bar{c} = \sqrt{2}$. These values, in turn, put the factors $4/3$ and the $\sqrt{2}$ in the denominator of the equation for L. Hence were the expression above the true one for the relative velocity considering a σ_1 molecule moving among σ_2 molecules, L_1 would become

$$L_1 = \frac{1}{\pi\sigma_a^2 N \frac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_1}}.^*$$

For L_2, the mean free path of a σ_2 molecule moving among σ_1 molecules, the expression would be

$$L_2 = \frac{1}{\pi\sigma_a^2 N \frac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_2}}.$$

It now happens that if the rigorous analysis be carried through assuming a Maxwellian distribution of velocities with average velocities $\bar{c}_1$ and $\bar{c}_2$ for the molecules, the integrations for the average relative velocities, assuming all angles of motion of σ_1 molecules and σ_2 molecules, yield a relative velocity $\bar{r} = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$. This, strangely, is the value found to be the case for the motions at right angles only. The detailed analysis of the strict averaging is, however, too lengthy for inclusion in this text, and reference should be made to the noteworthy deduction as given in the appendix of O. E. Meyers' "Kinetic Theory of Gases."[2] It is of interest to observe that if $\bar{c}_1 = \bar{c}_2$ this term gives the Maxwell free path.

One more case of interest now demands attention and that is the question of the free path of a σ_1 molecule in a gaseous mixture of N_1 molecules of the σ_1 type and N_2 molecules of the σ_2 type per cm^3. To get this, one can reflect that $\bar{c}_1$, the average velocity of the σ_1 molecule, divided by L_{12}, the mean free path of that molecule in the mixture, gives the number of molecular encounters Γ_1

* Since $\frac{1}{2}m_1\bar{c}_1^2 = \frac{1}{2}m_2\bar{c}_2^2$ the values of the c_1, $\bar{c}_2$ terms can be replaced by expressions in terms of m_1 and m_2, thus simplifying the expressions.

per second of a σ_1 molecule with σ_1 and σ_2 molecules. If there are N_1 of the molecules in a cm^3, the σ_1 molecule will collide with

$$\frac{\bar{c}_1}{L} = \pi \bar{c}_1 \sqrt{2} \sigma_1^2 N_1$$

of molecules of its own kind per second. If there are N_2 of the σ_2 molecules in a cm^3 the σ_1 molecule will collide with $\frac{\bar{c}_1}{L_1} = \bar{c}_1 \pi \sigma_a^2 N_2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$ $\bar{c}_1$ of the σ_2 molecules per second. Thus the number of impacts per second of the σ_1 molecule will be

$$\Gamma_1 = \sqrt{2} \pi N_1 \bar{c}_1 \sigma_1^2 + \pi \sigma_a^2 N_2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}.$$

Since $L_{12} = \frac{\bar{c}_1}{\Gamma_1}$, then

$$L_{12} = \frac{1}{\sqrt{2} \pi N_1 \sigma_1^2 + \pi N_2 \sigma_a^2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_1}.$$

Similarly, the mean free path L_{21} of the σ_2 molecules in the mixture will be

$$L_{21} = \frac{1}{\sqrt{2} \pi N_2 \sigma_2^2 + \pi N_1 \sigma_a^2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}/\bar{c}_2}.$$

39. Mean Collision Frequency of Molecules of a Given Speed, Mean Free Path of Such Molecules, Tait's Free Path.—In Sec. 37 the Maxwell free path for molecules moving with a Maxwellian distribution of velocities was deduced. This deduction gave the mean free path by dividing the average speed $\bar{c}$ by the mean numbers of collisions per second averaged over all molecules. The deduction was made by computing the average value of the collision frequency for molecules moving with a Maxwellian distribution, and dividing this into $\bar{c}$. The process by which this was accomplished can be seen in Secs. 18 and 37, where it is deduced. The matter may be regarded in another light, however, which leads to different results. It is obvious that the collision frequency Z must depend on the velocity of the molecule considered. If one can calculate Z, this frequency for a molecule of speed c, then one can calculate the mean free path of a molecule of speed c among the other molecules moving with Maxwell's distribution of velocities. This will lead to a value for the mean free path L_c of a molecule of velocity c. It is of importance to know this quantity for such a molecule, and it will, accordingly, be calculated in what follows. Having this, it is then possible to

determine the *average value of L for L_c averaged over all possible speeds.* Such an average path, designated by L_r, is numerically different from the *ratio* of the averaged velocity and collision frequency of Maxwell. As both are used in calculations, it is essential to know both values. Different modes of averaging are appropriate to the different problems of kinetic theory in which the mean free path plays a part, just as variously averaged speeds are useful in discussions involving the molecular speeds. It may be pointed out that the Maxwell free path is the one commonly used by physicists in developing approximate discussions along kinetic-theory lines because of its simplicity. The legitimacy depends on the particular use of the free path, though Tait's complex free path is in most cases the more accurate.

If the attention be fixed on those molecules which have a particular speed, it is evident that the mean number of collisions per second of such molecules with all others will depend on the speed of the molecules under consideration. The evaluation *of this mean number of collisions per second*, Z, for molecules of speed c moving in a gas in which the most probable molecular speed is α will now be carried out.

On the average, a molecule of speed c will collide in unit time with all of the molecules of speed c' contained in a cylinder whose base is $\pi\sigma^2$ and whose height is the relative velocity

$$V_r = \sqrt{c^2 + c'^2 - 2cc' \cos\theta},$$

θ being the angle between c and c'. Choose polar coordinates having the direction of c as axis, then θ and ϕ give the direction of the velocity of the other molecule c'.

By Sec. 34 the number of molecules in unit volume for which c' lies between c' and $c' + dc'$, θ between θ and $\theta + d\theta$, and ϕ between ϕ and $\phi + d\phi$ is

$$\frac{N}{\pi^{3/2}\alpha^3} c'^2 e^{-\frac{c'^2}{\alpha^2}} dc' \sin\theta d\theta d\phi,$$

so that the mean number of collisions per second will be

$$\frac{N\sigma^2}{\alpha^3\sqrt{\pi}} V_r c'^2 e^{-\frac{c'^2}{\alpha^2}} dc' \sin\theta d\theta d\phi.$$

The total number of collisions per second experienced by a molecule of speed c is obtained by integrating this with respect to c'

from 0 to ∞, to θ from 0 to π, and to ϕ from 0 to 2π. Integration with respect to ϕ is effected at once by merely writing in 2π for $d\phi$. Integration with respect to θ may be conveniently carried out by using the relative velocity as variable. One has

$$V_r dV_r = cc' \sin\theta d\theta.$$

Making these substitutions, the total number of collisions per second experienced by a molecule of speed c may be expressed by

$$\frac{2\sqrt{\pi}N\sigma^2}{\alpha^3}\frac{c'}{c}V^2{}_r e^{-\frac{c'^2}{\alpha^2}}\, dc'dV_r.$$

The integration limits with respect to V_r are as follows:

	$c' < c$	$c' > c$
$\theta = 0$	$V_r = c - c'$	$V_r = c' - c$
$\theta = \pi$	$V_r = c + c'$	$V_r = c' + c$

so that integration with respect to V_r yields two different expressions according to the relative sizes of c' and c. These are

$$\int V_r{}^2 dV_r = \frac{1}{3}[V_r{}^3] = \begin{cases} \frac{2}{3}c'(c'^2 + 3c^2) & c' < c \\ \frac{2}{3}c(c^2 + 3c'^2) & c' > c \end{cases}.$$

The total number of collisions is now to be obtained by integrating over all values of c' from 0 to ∞, using the appropriate integral according as $c' < c$ or $c' > c$, *i.e.*,

$$Z = \frac{\sqrt{\pi}N\sigma^2\alpha^2}{c}\left[\frac{4}{3}\int_0^c \frac{c'^2}{\alpha^5}(c'^2 + 3c^2)e^{-\frac{c'^2}{\alpha^2}}dc' + \frac{4}{3}\frac{c}{\alpha^5}\int_c^\infty c'(c^2 + 3c'^2)e^{-\frac{c'^2}{\alpha^2}}dc'\right].$$

It will be observed that the terms in the brackets are physically dimensionless. They form a function of a variable $x = c/\alpha$ defined by means of integration with respect to the variable $y = c'/\alpha$. The factor outside the brackets has the dimensions of reciprocal time as it should have.

The mean number of collisions per second is thus:

$$Z = \sqrt{\pi}N\sigma^2\alpha \cdot \frac{\Psi(x)}{x},$$

in which $\Psi(x)$ stands for the terms in brackets, *i.e.*,

$\Psi(x) = \frac{4}{3}\int_0^x (y^4 + 3x^2y^2)e^{-y^2}dy + \frac{4}{3}\int_x^\infty (x^3y + 3xy^3)e^{-y^2}dy$, and $x = \frac{c}{\alpha}$.

This function can be reduced to somewhat simpler terms by means of the integration formula

$$\int x^n e^{-x^2}dx = \frac{n-1}{2}\int x^{n-2}e^{-x^2}dx - \frac{1}{2}x^{n-1}e^{-x^2},$$

the result being

$$\Psi(x) = xe^{-x^2} + (2x^2 + 1)\int_0^x e^{-y^2}dy.$$

From this formula values of $\Psi(x)$ and related functions have been computed and may be found in tables.[3]

The result of the analysis is this: The mean number of collisions per second experienced by a molecule of speed $c = x\alpha$, where α is the most probable speed, is given by

$$Z = \sqrt{\pi}N\sigma^2\alpha\frac{\Psi(x)}{x},$$

where the factor $\frac{\Psi(x)}{x}$ can be obtained from the tables.

Thus the mean collision frequency of molecules of a given speed has been found to depend on the particular speed of the molecules considered. Their mean free path, similarly, depends on the speed, since

$$L_c = \frac{c}{Z},$$

in which c is the speed and Z the mean collision frequency of the molecules chosen.

Applying the expression for Z from above the result is, for L_c, the mean free path of the molecules of speed c in a gas in which the most probable speed is α:

$$L_c = \frac{x^2}{\sqrt{\pi}N\sigma^2\Psi(x)}$$

wherein $x = c/\alpha$.

This formula might be written:

$$L_c = \frac{1}{\pi N\sigma^2}\cdot\frac{\sqrt{\pi}x^2}{\Psi(x)},$$

in which form it is recognized that the first factor is the Clausius free-path formula for the case where all the molecules are at rest save the one whose free path is under consideration (Sec. 16). This corresponds to the free path in the present analysis of a molecule for which x is very large. The second factor may thus be regarded as a correction factor which allows for the fact that the molecule under consideration does not move with infinite speed with respect to the others. Values for the second factor may be found in tables.[3]

Starting with the assumption of a free path varying with the speed as deduced above, Tait calculated a new *mean* free path. Tait's calculation of the mean free path differs from that of Maxwell in that it starts from the formula for the mean free path of molecules of a given speed c and averages the values of L_c, weighting them according to the distribution of velocities. Tait's free path is thus given by:

$$L_T = \frac{1}{\pi N\sigma^2}\int_0^\infty \frac{4x^4e^{-x^2}dx}{\Psi(x)}.$$

The definite integral occurring here has been computed by Tait, who finds the value 0.677, so that the Tait free path is

$$L_T = \frac{0.677}{\pi N\sigma^2}.$$

It is important to see why Tait's free path differs from that of Maxwell. Examination of the derivations of the two that have been given will show that Maxwell's free path is obtained by dividing $\bar{c}$, the *mean* speed, by Z, the *mean* number of collisions per second averaged over all the molecules. On the other hand, Tait takes the value of the free path c/Z appropriate to each speed and averages this over all the molecules. Obviously, still another free path would be obtained if the mean value of the speed $\bar{c}$ were to be multiplied by the value of $1/Z$ averaged over all the molecules, and still others could be obtained by averaging in different ways. These will all depend on $1/N\sigma^2$ for their order of magnitude but will differ in the value of the numerical factor for much the same reason that the root-mean-square speed of the molecules is not the same as the arithmetic mean of the speeds.

40A. Number of Molecules Striking Unit Surface per Second. An excellent illustration of the application of the distribution law

is given by the rigorous calculation of the number of molecules striking unit surface per second. Take an element of surface ds, and consider an element of volume dv with N molecules per cm^3 in it. Then in dv there are Ndv molecules. This volume is r cm from ds along a line making an angle θ with the normal to ds (Fig. 21). The volume dv may then be written $dv = dr \times rd\theta \times r \sin \theta d\phi$. Of these $Nr^2 \sin \theta d\theta d\phi dr$ molecules, the number which have a velocity between c and $c + dc$ are, by Maxwell's law,

$$\frac{4}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc N r^2 \sin \theta d\theta d\phi dr.$$

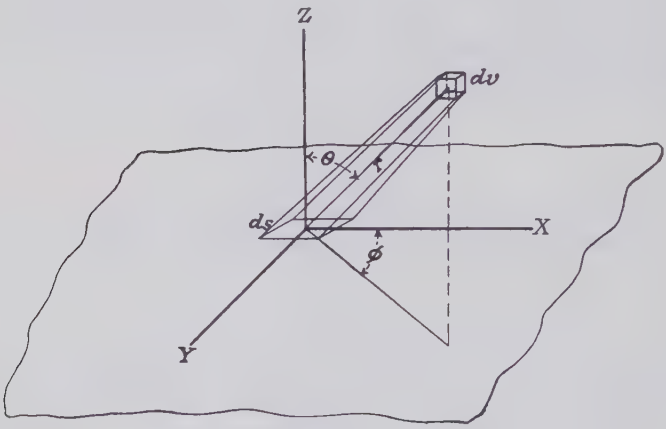

FIG. 21.

Now each of these starts a *new path* $B = \bar{c}/L$ times a second, where $\bar{c}$ is the *average speed*, and L is the mean free path. The number that leave dv per second moving towards ds with a velocity between c and $c + dc$ is B times the number of molecules above. Of these only the molecules emitted in the solid angle subtended at dv by ds will reach ds. This fraction is given by the ratio of the area $ds \cos \theta$ to the total surface of the sphere $4\pi r^2$ which molecules from dv going a distance r penetrate. The number of molecules that leave dv and that are headed for ds is given by

$$\frac{4NBc^2}{\alpha^3\sqrt{\pi}} e^{-\frac{c_2}{\alpha^2}} dc r^2 \sin \theta d\theta d\phi dr \frac{ds \cos \theta}{4\pi r^2}.$$

But of those headed for ds only those cross it that go a distance r or more without an impact. The fraction going r or more without an impact is given from the law for the distribution of free paths as $e^{-\beta r}$, where

$$\beta = \frac{1}{L} = \frac{B}{\bar{c}}.$$

Hence the number of molecules leaving dv per second that strike ds is given by

$$N_{dvdsd\theta} = \frac{4NB}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} c^2 dc r^2 \sin\theta d\theta d\phi dr \frac{ds\cos\theta}{4\pi r^2} e^{-\beta r}.$$

The number which strike ds per second from the whole space above is obtained by integrating r from 0 to ∞, θ from 0 to $\pi/2$, ϕ from 0 to 2π, and c from 0 to ∞. Hence the number of molecules striking ds per second from above is

$$N_{ds} = \frac{N}{\alpha^3\pi^{3/2}} \int_0^\infty c^2 e^{-\frac{c^2}{\alpha^2}} dc \times B \int_0^\infty e^{-\beta r} dr \int_0^{\frac{\pi}{2}} \sin\theta\cos\theta d\theta \int_0^{2\pi} d\phi ds$$

$$= \frac{N}{\alpha^3\pi^{3/2}} \left(\frac{\alpha^3\pi^{1/2}}{4}\right) B \left[\frac{-1}{\beta} e^{-\beta r}\right]_0^\infty \times \frac{1}{2} \times 2\pi ds.$$

Since $\beta = \frac{B}{\bar{c}}$,

$N_{ds} = \frac{N\bar{c}}{4} ds$, where $\bar{c}$ is the average speed. $\frac{N_{ds}}{ds} = \nu$ is the number striking 1 cm²/sec., so that

$$\nu = \frac{N\bar{c}}{4} = \frac{NC\sqrt{8/3\pi}}{4} = \frac{NC}{\sqrt{6\pi}}.$$

An interesting application of this law may be made to aid in calculating the vapor pressure of a substance. This has actually been done by Langmuir.[4] Quoting from a paper by Langmuir:

> Let us consider a surface of metal in equilibrium with its saturated vapor. According to the kinetic theory, we look upon the equilibrium as a balance between the rate of evaporation and rate of condensation. That is, we conceive of the time processes as going on simultaneously at equal rates.
>
> At temperatures so low that the vapor pressure of a substance does not exceed a millimeter, we may consider that the actual rate of evaporation of a substance is independent of the presence of vapor around it.

This merely means that the presence of atoms or molecules of the vaporizing substance at a mm pressure does not interfere with evaporation by acting as a reflecting layer that throws the evaporating molecules back to the surface on their first free path. This action is not taken into account in deducing the equation above, "that is, the *rate of evaporation* in a high vacuum is the same as the rate of evaporation in the presence of the saturated vapor" under these conditions. "Similarly, we may consider that the rate of condensation is determined only by the pressure of the saturated vapor." To see how this works the equation may be transformed as follows. Multiply $\nu = N\bar{c}/4$ by m, the mass of a molecule, then $m\nu$ is the weight w of substance striking a cm^2 of surface per second and thus also evaporating. Thus

$$w = m\nu = \frac{Nm\bar{c}}{4} = \frac{\rho\bar{c}}{4},$$

where Nm is the density ρ. But $\rho = \frac{M}{V} = \frac{Mp}{pV} = \frac{Mp}{RT}$, where p is the pressure, and M is the mass of vapor in volume V of a mol. Also $C = \sqrt{\frac{3p}{\rho}}$, and as $\bar{c} = \sqrt{\frac{8}{3\pi}}\, C$, then $\bar{c} = \sqrt{\frac{8p}{\pi\rho}} = \sqrt{\frac{8p}{\pi Mp/RT}} = \sqrt{\frac{8RT}{\pi M}}$. Therefore

$$w = \frac{1}{4}\frac{Mp}{RT}\sqrt{\frac{8RT}{\pi M}} = p\sqrt{\frac{M}{2\pi RT}}$$
$$= 43.74 \times 10^{-6}\, p\sqrt{\frac{M}{T}}.$$

Here M is the molecular weight, T is the absolute temperature, p is in dynes per cm^2, and w is the weight evaporated per cm^2 per second. For tungsten at 2800°abs., Langmuir found w, the loss in weight, to be 0.43×10^{-6} gram, per cm^2 per second. This gives $p = 28.6 \times 10^{-6}$ mm of Hg as the vapor pressure of W at this temperature.

40B. The Law of Evaporation of Molecules from a Liquid Surface.—At this point it is possible with little effort to deduce the law for the evaporation of molecules from a liquid surface. The law to be deduced is well known to students of physical chemistry who are familiar with its thermodynamical derivation. Kinetic theory permits the derivation of the law in a manner

giving a mechanical picture of the process. In addition the derivation leads to some important general conclusions which should appropriately be introduced at this point. The treatment in essence is taken from Jellinek's "Lehrbuch der Physikalischen Chemie," vol. II, page 246.

Imagine a plane surface of liquid in *equilibrium* with its vapor. This demands that three conditions be fulfilled. The first is that from each side of the surface of the liquid as many molecules pass in one direction as in the other. That means that the rate of condensation equals the rate of evaporation. The second is that, as temperature equilibrium also exists, the kinetic energy carried through the surface in one direction equals that carried through in the other. The third condition is that as much momentum be carried through the surface per second in one direction as another. This demands an equality of pressure. Without analyzing the nature of the transition layer between a homogeneous gas and a homogeneous liquid it can be assumed that in the transition layer there is a continuous variation of density between the two phases. Furthermore, the vapor will be, for simplicity, treated as an ideal gas. As a result of the capillary forces at the surface such as Laplace and Van der Waals assumed, molecules in the transition layer will experience a force. This force is such as to hinder the evaporating molecules and to draw in the condensing ones. In order to analyze the problem further, it must be assumed that all molecules are alike and that the volumes of the molecules can be neglected. It must also be assumed that Maxwell's distribution law holds for the molecules of the liquid as well as for the gas.

From the principle of equality of mass assumed above (for equality in the number of molecules carried implies equality of mass transported for molecules all of one kind), the first equation may be set up. Assume the x-axis to be normal to the surface and call the velocity component along the axis u. The number of molecules with a velocity between u and $u + du$ is then given by Maxwell's distribution law as

$$\frac{N_D}{\alpha_D \sqrt{\pi}} e^{-\frac{u^2}{\alpha_D^2}} du,$$

where α_D is the most probable speed of the vapor molecules, while N_D is the number of molecules per cm^3 of vapor. The

number of molecules of this speed crossing a cm^2 of surface per second from the vapor phase is, then,

$$\frac{N_D}{\alpha_D\sqrt{\pi}} ue^{-\frac{u^2}{\alpha_D{}^2}} du.$$

In crossing the transition layer these molecules get an increase in kinetic energy of $\frac{1}{2}ms^2$ from the surface forces. Thus since all molecules moving in the direction of the surface will be aided in crossing the surface layer, the number of molecules of all speeds that cross is

$$\frac{N_D}{\alpha_D\sqrt{\pi}} \int_0^\infty ue^{-\frac{u^2}{\alpha_D{}^2}} du = \frac{N_D\alpha_D}{2\sqrt{\pi}}.$$

For the molecules starting from below the surface layer upwards there is the similar expression

$$\frac{N_F}{\alpha_F\sqrt{\pi}} \int_0^\infty ue^{-\frac{u^2}{\alpha_F{}^2}} du.$$

In this equation N_F represents the number of molecules in a cm^3 of the liquid phase and α_F the most probable speed of the liquid molecules. Whether α_F and α_D are the same can be left undecided for the present. Now the molecules that start outward have to do work against the surface forces in order to escape. Also, as they expand from the specific volume of the liquid phase to that of the gaseous phase, in escaping they must do work against the Van der Waals' a/v^2 forces if they are present. Both these amounts of work may be lumped into a single term, and this must be equivalent to saying that in escaping from the surface the molecules lose as much kinetic energy, on the average, as the condensing molecules gain. That is to say, they lose on the average an energy $\frac{1}{2}ms^2$. Thus only the molecules having speeds greater than the s of the $\frac{1}{2}ms^2$ out of the number above that start outward will be able to escape. The energy $\frac{1}{2}ms^2$ will, in fact, be nothing other than the latent heat of vaporization per molecule, or λ/N_A, where λ is the heat of vaporization of a gram-molecule and N_A is the Avogadro constant. Thus the

number of molecules escaping from the surface per second, that is evaporating, is given by

$$\frac{N_F}{\alpha_F\sqrt{\pi}}\int_s^\infty ue^{-\frac{u^2}{\alpha_F{}^2}}du = -\frac{N_F\alpha_F}{2\sqrt{\pi}}e^{-\frac{s^2}{\alpha_F{}^2}}.$$

Since mass equilibrium exists, then, at once,

$$N_D\alpha_D = N_F\alpha_F e^{-\frac{s^2}{\alpha_F{}^2}}.$$

In an exactly similar manner the *energy* carried through the surface from both sides may be computed. In this case, however, the number transported must be multiplied by the energy transported in each case. Thus from the vapor side the energy transport for all velocities is given by

$$\frac{N_D}{\alpha_D\sqrt{\pi}}\int_0^\infty ue^{-\frac{u^2}{\alpha_D{}^2}}du \cdot \frac{1}{2}mu^2 = \frac{N_Dm\alpha^3{}_D}{4\sqrt{\pi}}.$$

From the liquid side the energy transport per cm^2 per second into the layer is

$$\frac{N_Fm}{2\alpha_F\sqrt{\pi}}\int_s^\infty u^3e^{-\frac{u^2}{\alpha_F{}^2}}du = \frac{N_F\alpha_F}{2\sqrt{\pi}}e^{-\frac{s^2}{\alpha_F{}^2}}\left\{\frac{1}{2}ms^2 + \frac{1}{2}m\alpha_F{}^2\right\}.$$

Of this energy $\frac{1}{2}ms^2$ is lost to the work of evaporation, thus the kinetic energy transported outward into the gas from the surface is

$$\frac{N_F\alpha_F}{2\sqrt{\pi}}e^{-\frac{s^2}{\alpha_F{}^2}}\frac{1}{2}m\alpha_F{}^2.$$

Equilibrium requires that

$$N_D\alpha_D{}^3 = N_F\alpha_F{}^3e^{-\frac{s^2}{\alpha_F{}^2}}.$$

At the same time, however, it was also found that

$$N_D\alpha_D = N_F\alpha_Fe^{-\frac{s^2}{\alpha_F{}^2}}.$$

holds. These two statements can only be true *if* $\alpha_D = \alpha_F$.*

* Jaeger[34] shows through precisely the same argument that for a gas in equilibrium in a *gravitational* field the quantity α at two points in the gas is the same. Hence in a *gravitational* force field *the temperature at equilibrium is uniform* (see page 92).

It is also necessary to show that, in spite of the fact that only the molecules that have higher speeds can leave the liquid (for they lose energy in getting out) while those with all speeds can enter it, the Maxwell distribution is maintained on both sides. This is proved if it can be shown that the one phase loses as many molecules of a given velocity per unit time as it gains from the other phase.

The number of molecules of velocity component normal to the surface between u and $u + du$ lost by the vapor phase in unit time is

$$\frac{N_D}{\alpha\sqrt{\pi}} u e^{-\frac{u^2}{\alpha^2}} du,$$

where $\alpha = \alpha_D$, the common speed. The number of molecules from the liquid phase which replaces these per cm^2 per second is

$$\frac{N_F}{\alpha\sqrt{\pi}} u_1 e^{-\frac{u_1^2}{\alpha^2}} du_1,$$

where u_1 is the velocity of the molecules leaving the liquid phase which are destined to have a velocity u on passing through the transition layer; that is, $u_1^2 - s^2 = u^2$. Substituting the value for u_1 gives at once

$$\frac{N_F}{\alpha\sqrt{\pi}} (u^2 + s^2)^{\frac{1}{2}} e^{-\frac{u^2+s^2}{\alpha^2}} \cdot (s^2 + u^2)^{-\frac{1}{2}} u du.$$

In order then that Maxwell's law be maintained, it is required that the expressions above be equal. Equating them, one has the condition as

$$N_D = N_F e^{-\frac{s^2}{\alpha^2}}.$$

That this condition is fulfilled follows at once from the equality of mass transfer which reads

$$N_D \alpha_D = N_F \alpha_F e^{-\frac{s^2}{\alpha_F^2}},$$

provided $\alpha_D = \alpha_F = \alpha$, which is the case.

Finally, pressure equality requires that

$$N_F \alpha_F^2 e^{-\frac{s^2}{\alpha_F^2}} = N_D \alpha_D^2.$$

As this confirms the previous deduction, it is merely of passing interest and is given to show that all three conditions are mutually in agreement. The expression

$$N_D = N_F e^{-\frac{s_2}{\alpha^2}},$$

however, gives the equilibrium condition for evaporation. Now both N_D and N_F may be multiplied by m, the mass of a molecule, and each member of the ratio $\frac{s^2}{\alpha^2}$ by $\frac{N_A m}{2}$, where N_A is the Avogadro number and m is the mass of the molecules. The equation then becomes

$$mN_D = mN_F e^{-\left(\frac{\frac{N_A m}{2} s^2}{\frac{N_A m}{2} \alpha^2}\right)}$$

But $\frac{N_A m}{2} s^2$ is nothing else than λ, the latent heat of evaporation per gram-molecule, while $\frac{N_A m}{2} \alpha^2$ is nothing else than RT, for $N_A \frac{m}{2} \alpha^2 = N_A \frac{m}{2} \frac{2}{3} C^2 = RT$. Also mN_D and mN_F are the densities of gas ρ_D and liquid ρ_F. One thus has

$$\rho_D = \rho_F e^{-\frac{\lambda}{RT}}.$$

This can be transformed readily into $\lambda = RT \log_e \frac{\rho_F}{\rho_D} = RT \log_e \frac{v_D}{v_F}$, where v_D and v_F are the molecular volumes of gas and liquid. This equation may also be deduced from thermodynamic reasoning. In the latter case it differs slightly, and this is due to the omission of certain factors in the kinetic-theory deduction, which were omitted for the sake of simplicity (*i.e.*, the assumption of an ideal gas). The neglect of cohesive forces in the deduction would not change anything except that the $\frac{1}{2}ms^2$ would, as stated before, have to contain the work against the a/V^2 term of Van der Waals' equation. The neglect of the volumes of the

molecules would play some rôle. The case was treated by Kammerlingh-Onnes.[50] The effect of the volumes of the molecules would result in a reduction of the number of the molecules starting outward which escape, due to the "shadowing" of the surface by molecules in the transition layer. In this case, however, the molecules struck by molecules which would escape are capable of escaping, so that the effect of the volumes of the molecules in this sense is negligible. Were foreign molecules present, this would not be so. However, a consequence of this must be considered. If a row of molecules normal to the surface be considered and one molecule with an energy u necessary for escape strikes the innermost one, the outermost one will receive the necessary energy to escape if the impacts are perfectly elastic, central, and the masses are equal. Since, however, the rigidity of the molecules is great, the time taken for the end molecule to escape after the inner one is struck would be less than would have been the case for the initial molecule to have moved freely down the chain of molecules. If the time of travel of the molecular impulse through a molecule be negligible, then the time of escape by the "chain of impacts" mechanism would be shorter. The time would be less in the ratio $\frac{u}{u + z\sigma}$, where u is the distance gone in 1 sec of free movement and $z\sigma$ is the length of path covered inside the molecules lying in the path u cm long, there being z molecules in the row of u cm length in the gas and σ being the diameter of a molecule. If the collisions of all sorts be averaged as well as relative motions, analysis yields the apparent velocity of the molecules as $u\frac{v}{v - b}$ where v is the volume of the gas and b is the Van der Waals' b. The change in the theory above produced by the use of $u\left(\frac{v}{v - b}\right)$ in place of u gives as a final equation

$$N_D \frac{v_D}{v_D - b_D} = N_F e^{-\frac{s^2}{\alpha^2}} \frac{v_F}{v_F - b_F},$$

which gives

$$e^{\frac{\lambda}{RT}} = \frac{v_D - b_D}{v_F - b_F},$$

or

$$\lambda = RT \log \frac{v_D - b_D}{v_F - b_F}.$$

This equation is in perfect agreement with the thermodynamically deduced equation for condensation. In practice, however, it is simpler to use the approximate equation for an ideal gas.

41. Experimental Verification of the Maxwellian Distribution of Velocities.—Since the first edition of this text was published, direct evidence of the Maxwellian distribution of velocities has been obtained in striking form. Previous to this, two indirect types of verification had been obtained. The earliest type of verification depended on the fact that in the broadening of the spectral lines of light emitting atoms[8,9,10,11,36] the velocity distribution plays an important rôle. Again it was shown by Knudsen[37] that the rate of effusion of molecules through small openings could be deduced theoretically, the rate depending for its numerical value among other things on the form of the distribution law. In both the Doppler broadening of spectral lines and the rate of effusion, the effect of the form of the distribution law is to alter the value of a numerical coefficient which can be evaluated by a comparison of theory and experiment. If the observed and calculated coefficients agree within the limits of error, the law can be considered as established. Such coefficients are very insensitive to variations in the form of the law (*e.g.*, for effusion the effect of the Maxwellian distribution causes a difference in the constant relative to the case for uniform velocities of but 8.6 per cent with an experimental error of the order of 3 per cent). Both these investigations have indicated the existence of an approximation to a Maxwellian distribution of velocities.

The second type of test of the distribution which quantitatively should be accurate over a very large range is the measurement of the distribution of the velocities of the electrons emitted by a hot body.[6] The thought underlying this phenomenon was that electrons were free inside the metal lattice and were subject to the Maxwellian distribution of velocities. Such electrons are held in the metal by the forces of attraction of the positive ions of the metal lattice at the surface. Thus, to escape, the electron must do work against the potential existing at the metal surface. If the potential is ϕ volts and e is the electron, then the escaping electron velocity u normal to the metal surface must be greater than u_0 defined by the equation $\chi = \phi e = \frac{1}{2}mu_0^2$. All electrons

crossing 1 cm^2 of metal surface per second with a normal component of velocity greater than u_0 will give rise to the thermionic current. The components of the velocities of the electrons emitted by the surface then must have a distribution of velocities derived from the Maxwellian lying between 0 and ∞, which, as shown in Sec. 40*B*, is unchanged by escaping against the attracting forces. Since electrons can have the normal component of their velocities accurately measured by retarding fields, a study of the emission would constitute an accurate check on the shape of the high-velocity side of the distribution curve. Actually such a check over a great range of velocities and of high precision has been achieved despite the fact that it has in recent years been shown to be almost certain that inside the metal, even at fairly high temperatures, the energy distribution of the electrons as a whole is far from Maxwellian[38,39,40]. Owing, however, to the fact that only those electrons which have a high enough energy to escape are the non-degenerate electrons, which have a Maxwellian distribution, the Maxwellian distribution for the escaping electrons is proved and we can consider this investigation to be an accurate check on the distribution law in the high-velocity range.

The direct verification of the Maxwell distribution law came as the development of Stern's[5] molecular-beam-velocity analyzer. The initial experiments of Stern were unable clearly to delineate the form of the curve. Later the work of Lammert[41] using the toothed-wheel[42,43] method and the perfection of the rotating-slit method as developed at the University of California[44,45] have supplied the necessary data. Another excellent confirmation came from the beautiful determination of the Bohr magneton by Meissner and Scheffers by means of magnetic deflection.[46] These verifications will be described in detail after certain preliminary concepts have been developed in the following section.

42. The Average Velocities of Molecules or Electrons Emitted from Hot Bodies.—If an enclosure containing atoms, molecules, or electrons in equilibrium at a temperature T is considered the distribution of velocities is at once defined by the evaluation of α (the most probable speed) from the temperature. Thus in Sec. 5 it was found that $pv = RT = \frac{1}{3}\nu mC^2$. Hence, dividing

by ν, the number of molecules present in the volume v, one can write $mC^2 = 3\frac{R}{\nu}T$. Calling $\frac{R}{\nu} = k$, one obtains $\frac{1}{2}mC^2 = \frac{3}{2}kT$.*

From the above, $C = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$, where m is the mass of a molecule and M is the mass of a gram-molecule, R being given for a gram-molecule. Since $\alpha\sqrt{\frac{3}{2}} = C$ or $\alpha = \sqrt{\frac{2kT}{m}}$, it is seen at once that the number of molecules having a velocity c in the enclosure is expressed by the equation

$$N_{dc} = \frac{4N}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{mc^2}{2kT}}dc. \quad \text{(See Sec. 36.)}$$

If a small opening be made in the enclosure so that the molecules can stream out into an evacuated space, the average velocity of the molecules emitted will not be the same as the average velocity of the molecules existing in the enclosure, as a little consideration will show. The molecules inside were in equilibrium. Those issuing are not, and the number issuing in unit time is the greater the greater the velocity of thermal agitation of the molecules, for it is only by virtue of their velocities that they can emerge. Hence the chance of a molecule emerging is proportional to its velocity. The number emerging at a given velocity c will then depend on the product of the number N_{dc} of particles of that velocity present and the value c of the velocity. Thus the average velocity in such a stream C_1 will not be that given by $C = \sqrt{\frac{3kT}{m}}$, but will be greater than this. It may be found as follows: In getting C^2 in Sec. 35 its value was obtained by multiplying N_{dc} by c^2, integrating it from zero to infinity and dividing it by the integral of N_{dc} from zero to infinity, which was N. To find the value of $C_1{}^2$ under the conditions of the emitted beam, the product of c^2 into the number of molecules N'_{dc} in the stream which have a velocity c, to wit cN_{dc}, must be integrated from zero to infinity and divided by the integral of the number of

* The quantity k is known as the Boltzmann constant and it is the value of the gas constant k per molecule in equilibrium. R is the gas constant for the number of molecules ν.

particles issuing with a velocity c (*i.e.*, cN_{dc}), taken from zero to infinity; that is, the value of C_1^2, the average in a stream, is given by

$$C_1^2 = \frac{\int_0^\infty \frac{4N}{\alpha^3\sqrt{\pi}} c^2 \times c \times c^2 e^{-\frac{c^2}{\alpha^2}} dc}{\int_0^\infty \frac{4N}{\alpha^3\sqrt{\pi}} c \times c^2 e^{-\frac{c^2}{\alpha^2}} dc} = 2\alpha^2.$$

In the inside of the oven $C^2 = \frac{3}{2}\alpha^2$, hence $C_1^2 = \frac{4}{3}C^2$, $C_1 = \sqrt{\frac{4C^2}{3}} = \sqrt{\frac{4kT}{m}}$. Thus the average velocity of the molecules in such a stream is $C_1 = \sqrt{\frac{4kT}{m}}$ in contrast to the root mean square value $C = \sqrt{\frac{3kT}{m}}$ inside the oven.

43. The Rate of Escape of Molecules from a Hot Surface.— In one of the proofs of the distribution law it will be essential to know the number of molecules or electrons escaping from a heated surface having a component of velocity u normal to the surface. Thus it seems of interest to investigate this point in what follows. In this discussion the molecules below a bounding surface may be assumed in equilibrium with a source of energy. A certain number of these are passing outward each instant in virtue of their heat motions. The number of such that leave may be found as follows: It is obvious that the component of velocity u normal to the surface is the only one effective in driving them through it. If there *are N molecules per cm*^{3} present, the number with a velocity component u which would strike an area ds in a time dt are those lying in a cylinder of length udt and base ds. That number is $Nudtds$. Of these N molecules per cm^3, only $f(u)du$ have a velocity between u and $u + du$. Hence, if ds is 1 cm and dt is 1 sec., the number of velocity u passing through 1 cm^2/sec. is

$$N_{(u)}du = \frac{Nu}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du.$$

For the type of applications to be made it is simpler to transform this equation by introduction of a new set of constants. Since these constants are frequently encountered in published papers,

their introduction will not be amiss at this point. It was found that in equilibrium $C^2 = \frac{3kT}{m}$. If one calls $h = \frac{1}{2kT}$, then $C^2 = \frac{3}{2mh}$. Since $C^2 = \frac{3}{2}\alpha^2$, therefore $\alpha = \sqrt{\frac{1}{mh}}$. The above equation then becomes

$$N_{(u)}du = N\left(\frac{hm}{\pi}\right)^{1/2} ue^{-hmu^2}du.$$

While $N_{(u)}du$ represents the number of molecules striking unit surface per second with the velocity u, the *total* number of molecules striking the surface with a velocity such that they can penetrate the surface is the integral of $N_{(u)}du$ from $u = 0$ to $u = \infty$. This number can be designated as η and is

$$\eta = \int_0^\infty N_{(u)}du = \frac{N}{2(\pi hm)^{1/2}}.$$

This gives N the number of molecules per cm^3 of gas in terms of η as

$$N = 2\eta(\pi hm)^{1/2},$$

so that one can write

$$N_{(u)}du = 2\eta hmue^{-hmu^2}du$$

which is a convenient form of the equation.

Hence the chance that a molecule will leave the surface in a gas with a velocity component between u and $u + du$ is given by $N_{(u)}du/\eta$ or

$$F(u)du = 2hmue^{-hmu^2}du.$$

It was shown in Sec. 40B that, in equilibrium, molecules escaping due to thermal agitation from a space across a boundary against which work is done, when once outside, maintain the Maxwellian distribution with the same average energy as before. Thus it is seen that the number of thermionically liberated electrons as a function of their velocity can be calculated at once from $F(u)du$ by integration between proper limits, as crossing the boundary does not modify the distribution law.

44. The Distribution of Velocities among Electrons Liberated from an Incandescent Source.—To calculate this distribution of electrons from an incandescent source on a classical basis one can proceed as follows. The number of molecules or electrons

of velocity components between u and $u + du$ normal to the surface striking the surface per second was given in Sec. 43 as $N_{(u)}du = \eta 2hmue^{-hmu^2}du$, where η is the total number of molecules or electrons striking unit surface per second. The number of molecules $N_{(v)}dv$ and $N_{(w)}dw$ with components v and w along the y- and z-axes parallel to the surface, which strike the surface, is not altered by the normal component and is thus given by the expressions of page 79 in the new terminology as

$$N_{(v)}dv = \eta\sqrt{\frac{hm}{\pi}}e^{-hmv^2}dv = \eta f(v)dv,$$

$$N_{(w)}dw = \eta\sqrt{\frac{hm}{\pi}}e^{-hmw^2}dw = \eta f(w)dw.$$

If the electrons, in order to escape, must overcome a potential of value ϕ at the surface, due to the positive ions of the metal lattice, then only electrons with a normal component of velocity u_0 or greater, given by $\frac{1}{2}mu_0^2 = \phi\epsilon = \chi$ will have the energy to escape, ϵ being the electronic charge. The current per cm^2 due to the escaping electrons will then be the charge ϵ into the sum of all electrons out of the η striking the surface per second which have an x-component of velocity greater than u_0 or an energy along x greater than χ (*i.e.*, the integral of the number with velocity components u from u_0 to ∞, v from $-\infty$ to $+\infty$ and w from $-\infty$ to $+\infty$). Hence the current i will be

$$\begin{aligned} i &= \eta\epsilon\int_{u_0}^{\infty}F(u)du\int_{-\infty}^{+\infty}f(v)dv\int_{-\infty}^{+\infty}f(w)dw \\ &= \eta\epsilon e^{-hmu_0^2} = \frac{N\epsilon}{2\sqrt{\pi hm}}e^{-hmu_0^2} \\ &= \frac{N\epsilon}{\sqrt{2\pi m}}(kT)^{1/2}e^{-\frac{mu_0^2}{2kT}} = \frac{N\epsilon}{\sqrt{2\pi m}}(kT)^{1/2}e^{-\frac{\chi}{kT}} \\ &= AT^{1/2}e^{-\frac{b}{T}}, \end{aligned}$$

where $b = \chi/k$ and $A = N\epsilon(k/2\pi m)^{1/2}$, a constant. N is the number of free electrons per cm^3, which for Ag is about 5.9×10^{22}. The constant b is the thermionic work function, and the form of the equation is that early deduced by Richardson[6,13,14] on a thermodynamic basis. In the form last given it has been accurately verified over a large range of values of i. The factor $(T)^{1/2}$ has *not* been verified in this range experimentally, as its

influence is so minute compared with the T in the exponential portion.

The experimental test of the law is relatively simple. It was first accomplished by O. W. Richardson[6] in the following manner. As has been shown, the energy distribution of the emitted electrons is derived from Maxwell's law and is that corresponding to the energy to be expected from this classical law at the temperature of the metal. The normal velocity component of the electrons which have escaped (Sec. 40B) is then that to be expected for escaping molecules *inside* the metal for the classical case. By placing opposite the hot metal source in vacuum as the other plate of a parallel plate condenser a plane electrode B connected to an electrometer or a galvanometer, electrons from the source will reach the plate B and give a current i (if the emission is not too great to cause space-charge effects). If between the source and B a potential of value V is applied opposing the flow of electrons (*i.e.*, B negative to the filament), only those electrons with a velocity component normal to the plates of value greater than $mu^2/2 = V\epsilon$ will reach B. If then one plots the current to B as a function of V, one will get the current for all electrons having a velocity greater than $u = \sqrt{2V\epsilon/m}$.

Now the current of electrons of these velocities exceeding a value of u_0 was found on the classical theory to be

$$i = \frac{N\epsilon}{\sqrt{2\pi m}}(kT)^{1/2}e^{-\frac{\chi}{kT}}$$

where $\chi = \frac{m}{2}u_0^2 = V\epsilon$. Calling $\frac{N\epsilon}{\sqrt{2\pi m}}(kT)^{1/2} = i_0$ the current when $V\epsilon = \frac{m}{2}u_0^2 = \chi = 0$, we can write at once $i = i_0 e^{-\frac{V\epsilon}{kT}}$. If one multiplies the top and bottom of $\frac{V\epsilon}{kT}$ by N_A, the Avogadro number, $\frac{N_A\epsilon}{N_A kT}V = \frac{N_A\epsilon}{R_A T}V$, and one can write the law in experimental form as $\log \frac{i}{i_0} = -\frac{N_A\epsilon}{R_A T}V$, where $N_A\epsilon$ is the Faraday constant and R_A is the well-known gas constant. Thus, if the distribution law of escaping electrons derived from Maxwell's law has the same form as the distribution of electronic velocities,

log i/i_0 plotted against V should give a straight line. Now Richardson and Brown carried out this measurement of i/i_0 as a function of V, and the results of one set of measurements are shown in Fig. 22. It is seen at once that the relation between log i/i_0 and V is a linear one, and careful measurements have shown this to hold within the limits of experimental error, which is 1 per

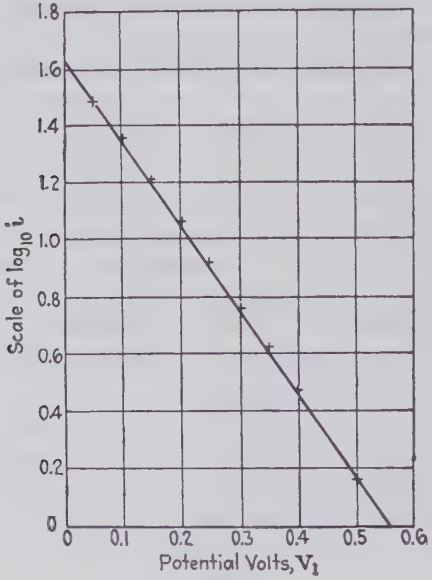

FIG. 22.

cent. Later measurements were made to verify the law for the components parallel to the emitting surface, and sufficiently close agreement was found to make this seem true if the results were taken in conjunction with the very nice verification in the case of the normal component.

Another equally important test to be obtained from these experiments was whether the average energy of the electrons was that to be expected from the distribution law and from the temperature of the filament, in other words, whether the electrons had the energy corresponding to the molecular energy of agitation at the emission temperature of the filament.

This can be tested easily as follows: If log i/i_0 be measured as a function of V, the constant factor $\frac{N_A\epsilon}{R_AT}$ can be determined

from the slope of the straight-line relation between log i/i_0 and V. If the temperature T be determined optically from the filament, then, since $N_A\epsilon$ is known, R_A can be determined from the experiments and compared with the known value.

Early experiments gave a fair agreement only in view of the great experimental difficulties to be surmounted.[15,16] Finally, Germer[17] made a most careful measurement for eight different temperatures from 1440 to 2475°K, which after correction for contact potential differences showed that the current varied with the voltage in just the manner calculated on the assumption that the electrons leave the filament with velocity components distributed in accordance with Maxwell's law for an electron atmosphere in temperature equilibrium with the hot filament. At 2475°K the assumed Maxwellian distribution was verified up to a retarding potential so great that only one in 10^{10} emitted electrons was able to reach the collector. The value of R_A, as found from the slope of the line for the value of T above, agreed with the well-known value of R_A within 1 per cent. Thus experimentally one can assert that the high-velocity side of the distribution-law curve has been verified with good precision over a rather large range.

In view of this rather striking confirmation, the statement previously made that the distribution function for electrons in the metal is *not* of Maxwellian form requires further study. Although the theoretical investigation belongs more properly in the field of statistical mechanics,[39] it is of interest to give the new law and discuss its bearing on the problem of thermionic emission in view of its increasingly wide application.

It has been shown by Sommerfeld[38,39] that, when at ordinary temperatures the light, free electrons[13,14] in a metal form a gas of numerical density 5.9×10^{22} electrons per cm^3 compared with the 2.7×10^{19} molecules per cm^3 ordinarily encountered in gases, one cannot assume that the ordinary distribution law holds. Applying the Fermi-Dirac statistics[38,39] and the exclusion principle of Pauli, it transpires that there is a limitation to the crowding of momentum and position vectors in the phase space representing the gas (see also page 449). This limitation says that no more than one molecular momentum vector, or two electron momentum vectors, can occupy a cell of volume h^3 in phase space. Here h is the Planck constant of quantum action. This means that with a low temperature and thus relatively

few Maxwellian momentum cells in phase space available the superfluous electrons take up cells of higher momentum than warranted by the temperature. Such electrons are called *degenerate* and have an average energy (temperature) well above that of the metal. They do not share in such typical temperature-dependent phenomena as the specific heat. With these statistics the probability of an electron having velocity components between u and $u + du$, v and $v + dv$, and w and $w + dw$ is

$$f(u)f(v)f(w)dudvdw = \frac{2m^3}{h^3} \frac{dudvdw}{e^{\left[\frac{m(u^2+v^2+w^2)}{2kT}+a\right]} + 1}.$$

When conditions comprising electron density, etc., are such that a is positive and much greater than unity, the value of a is given by

$$e^{-a} = \frac{nh^3}{2}(2\pi mkT)^{-3/2}.$$

The equation then at once reduces to the classical form of Maxwell, the gas is *non*-degenerate, and one has the familiar form

$$f(u)f(v)f(w)dudvdw = \frac{1}{\alpha^3\pi^{3/2}} e^{-\frac{m}{2}\frac{u^2+v^2+w^2}{kT}} dudvdw.$$

This occurs when e^{-a} is small and thus when n is small and T and m are large, *i.e.*, for a *normal* gas. In this case one can plot $f(u)f(v)f(w)dudvdw$ against $\frac{m}{2}(u^2 + v^2 + w^2) = \frac{mC^2}{2}$, as in Fig. 23, curve A. This form of the distribution law for the chance of a molecule having a given *vector* velocity differs as is seen from the chance of it having a given speed irrespective of direction as shown in Fig. 20.

For the case that a is negative, the equation can be rewritten in a more convenient form by putting $a = -\frac{\mu}{kT}$.

The distribution law then becomes

$$f(u)f(v)f(w)dudvdw = \frac{2m^3}{h^3} \frac{dudvdw}{e^{\left[\frac{m(u^2+v^2+w^2)-\mu}{2kT}\right]} + 1},$$

where $\mu = \left(\frac{3n}{\pi}\right)^{2/3} \frac{h^2}{8m}$. This equation takes a most interesting

form for small values of the variable $\frac{m}{2}(u + v^2 + w^2)$, for the exponential then becomes small compared with 1 and one has $f(u)f(v)f(w)dudvdw = \frac{2m^3}{h^3}dudvdw$, a constant. At $T = 0$, the curve for $f(u)f(v)f(w)$ takes on the form of the rectangle in Fig. 23, curve B. In this case the electron gas is entirely degenerate. At values of $\frac{m}{2}(u^2 + v^2 + w^2) > \mu$, the equation takes on a more and more Maxwellian form as the energy gets greater. The higher T, the greater the region of transition and for large T

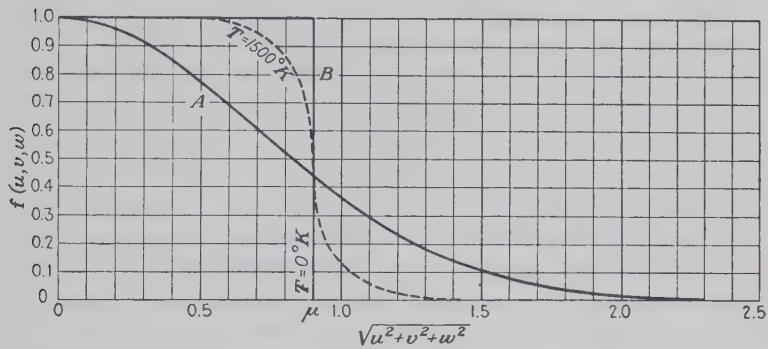

FIG. 23.

(*e.g.*, 1500°K for Ag) the curve takes on the form of the dotted line. In this case the *higher energy electrons* are not degenerate and the distribution is Maxwellian. At *very* high temperatures the curve must go over to the classical form of Fig. 23, curve A.

Conditions in metals with high electron densities and the small electron mass are such that the electrons are largely degenerate and it is only for energies $\frac{m}{2}(u^2 + v^2 + w^2) > \mu$ that at higher temperatures there is an approach to a Maxwellian distribution. Now it is precisely just those electrons with high energies, greater than μ, that will escape against the attractive forces, and these it is noticed are the ones that approach a Maxwellian distribution.

To deduce the value of the electron current per cm^2 in the case of the new distribution law, the procedure is precisely the same as that resorted to for the Maxwellian case, except that

it is more complicated. The evaluation of the number of electrons striking the surface per second with a velocity u must be carried out, and this component together with the y- and z-components is then to be integrated as before (see page 118). In this case the potential to be overcome by the electrons in order to leave the metal may be taken as ϕ_a, where $\phi_a \epsilon = W_a$. Integration gives as a final result that

$$i = \frac{4\pi\epsilon m}{h^3}(kT)^2 e^{-\frac{W_a - \mu}{kT}} = AT^2 e^{-\frac{b}{T}},$$

where $b = \dfrac{W_a - \mu}{k}$ and $A = \dfrac{4\pi\epsilon m}{h^3}k^2$.

For the case that $\mu/kT = a$, which is positive and greater than unity, one arrives at the equation deduced from Maxwell's law. If a is negative, the equation will be that given above. Comparing the latter equation with the classical equation, it is seen that it differs in several respects. The constant term A is radically different, containing the ~~Planck~~ h and *not* the concentration of free electrons. The current varies as T^2 instead of $T^{1/2}$, a point not amenable to experimental test. Finally, the symbol χ is found to be replaced by $W_a - \mu$. This is very interesting in that it says that χ does not represent the height of the energy required to escape from the metal but represents this energy less μ which is a measure of the *average energy* of the *degenerate electrons* that help push the electron out. The equation here deduced is almost identical with an equation rigorously deduced by Dushman[40] on thermodynamic grounds. If this equation contained an added factor D of value between 0 and 1, giving the average chance that an electron striking the surface would not be reflected back and would thus escape, and if $D = \frac{1}{2}$, the constant A of Dushman and the constant A above would be identical.

It must, however, be noted that the electrons are emitted at high temperatures only and that those emitted are only the electrons in the Fermi distribution whose energy exceeds $W_a = \mu + \chi$, *i.e.*, those electrons in the portion of the Fermi distribution which are *not* degenerate. They will then closely approach the Maxwellian distribution for energies $\frac{1}{2}mC^2$ greater than μ. Thus the experiments of Richardson[6] and Brown, and of Germer[17] lead to no contradiction with modern theory.

A further check of the equation beyond that given by Germer comes from the values of the total emission currents when *all* electrons emitted are caught by the galvanometer plate. This, according to the wave mechanics, should be

$$i_0 = 2ADT^2 e^{-\frac{W_a - \mu}{kT}},$$

where A is the theoretical value of the Dushman[40] constant, which is 60.2 amp./cm^2 deg^2. Now for a few pure metals the value of A observed is just this. For monatomic films of more electropositive metals the A observed is less than Dushman's value, and for similar films of electronegative elements the A observed is greater. In part these deviations may depend on the factor D, although there is at present no explanation for the very marked variation of some substances (*e.g.*, Pt). The question as to whether the factor T outside the exponential term should be $T^{1/2}$ or T^2 has not been answered by experiment, as the range over which the equation can be checked is too small relative to the large variation of $e^{-\frac{b}{T}}$ to give a test. The small temperature range is due to the fact that emission begins only above about 1100°K for most metals, and the metals all vaporize too rapidly above 3500°K. However, both the A and the variation with T^2 are derived from classical thermodynamics as well as from the new theory and so can be assumed to be correct. The fact that $\chi = b_0/k = W_a - \mu$ also receives some support. The refractive index of the metals for electron waves allows W_a to be roughly determined from electron diffraction. The value of μ can be computed from the electron density in metals, and, assuming that there are from two to three free electrons per atom, a plausible value from other data, it is possible to get values of μ which subtracted from W_a give values of χ in agreement with experiment. The values of χ observed from both thermionic and photoelectric effects, where comparable surfaces are obtainable, also agree fairly well as they should. One may therefore accept the verification of the Maxwellian distribution of velocities from these data as fairly satisfactory within the limitations imposed by theory.

45. The Verification of the Maxwell Distribution by the Doppler Effect in Spectral Lines.—As stated before, the Doppler effect causes a broadening of otherwise narrow spectral lines due to the components of molecular velocities toward and away

from the observer with the Maxwellian distribution of velocities imposed on the molecules.[7] If the original shape of the lines is known and if no other effects occur to cause a broadening, a measure of the broadening should give a means of comparing the observed broadening to one calculated on the basis of the assumption of a Maxwellian distribution of velocities. Unfortunately the shape of the spectral lines is not accurately known, and one must assume an approximate arbitrary shape. This is usually chosen as a uniform distribution over a small finite frequency interval for the sake of simplicity. Furthermore, it is very questionable whether the lines may not be broadened by other factors as well. Such factors would be the damping of the virtual oscillators through radiation (giving the natural line width), the mutual interaction of the atoms or molecules such as the Lorentz impact damping, the broadening and displacement due to fields of neighboring atoms, and broadening through the electromagnetic coupling of resonant atoms. The natural line breadth of course underlies all the phenomena. The effects of impacts and of interacting force fields can be reduced to a large extent by utilizing sources that have a maximum time between impacts (*i.e.*, long free paths) by working at low pressures. Thus conditions in a Geissler or glow discharge at low pressure furnish the most ideal circumstances for experimental study.

Assuming that one can work under ideal conditions, the problem may be considered briefly as follows: If two monochromatic radiations of the same frequency ν and amplitude a meet with a phase difference θ, the resulting intensity is given by $I = 4a^2 \cos^2 \frac{\theta}{2}$.[7,8] Since the path difference δ which the waves have undergone to get a phase difference θ can be written as $2\pi\frac{\delta}{\lambda} = \theta$ (*i.e.*, 2π multiplied by the number of wave lengths in δ), and since $\lambda = V/\nu$, where V is the velocity of light and ν is the frequency, the above expression becomes $I = 4a^2 \cos^2 \frac{\pi\delta}{V}\nu$. This means that the intensity of the light will vary as the path difference δ between the two radiations varies but will vary as the $\cos \frac{\pi\delta}{V}\nu$ for indefinitely great values of δ. If, however, the light from the source is not of a unique frequency but

varies continuously over a small range of frequencies in each case, say from ν_1 to ν_2, the ray must be divided into narrow portions corresponding to the interval $\Delta\nu$, for which the above expression can be used. In this case the amplitude a may vary with each $\Delta\nu$ chosen. The total intensity of the fringes in this case is $\int I d\nu = 4\int a^2 \cos^2 \frac{\pi\delta\nu}{V} d\nu$, where a^2 is a $f(\nu)$. If one choose a line of uniform intensity going from ν_1 to ν_2, the value of the integral above becomes

$$\int_{\nu_1}^{\nu_2} I d\nu = 2a^2(\nu_2 - \nu_1)\left[1 + \frac{\sin \frac{\pi\delta}{V}(\nu_2 - \nu_1)}{\frac{\pi\delta}{V}(\nu_2 - \nu_1)} \cos \frac{2\pi\delta}{V}\nu_0\right],$$

ν_0 being the middle of the band, $\frac{\nu_2 + \nu_1}{2} = \nu_0$. It is seen that as δ grows large, the expression

$$\alpha = \frac{\sin \frac{\pi\delta}{V}(\nu_2 - \nu_1)}{\frac{\pi\delta}{V}(\nu_2 - \nu_1)},$$

approaches 0, so that the $\int I d\nu$ instead of varying periodically with the $\cos \frac{2\pi\delta}{V}\nu_0$ for indefinitely large values of δ ultimately becomes constant as δ increases. Thus for small values of δ an interferometer with slightly tilted plates will show visible interference fringes across its plates, due to the small differences in δ as a result of the tilt. As δ varies, these fringes will move across the cross hairs of the observing telescope in a uniform manner, due to the cosine term. If, however, δ be made large so that α vanishes, there will be no change in intensity, for the 0 value of α annihilates the cosine term. The plates will therefore show a uniform illumination and the fringes will vanish. The vanishing of fringes is a more or less subjective determination, as it depends on the *contrast* or intensity difference between maxima and minima of the fringes. The ratio I_2/I_1, the maxima to the minima of the fringes, is given by $\frac{I_2}{I_1} = \frac{1 - \alpha}{1 + \alpha}$. Thus $\alpha = \frac{I_1 - I_2}{I_1 + I_2}$, which was defined by Michelson[9] as the *visibility*

of the fringes. If one can observe the value of δ for which the fringes vanish and know what value of α (*i.e.*, of I_2 and I_1) disappearance corresponds to, one can evaluate $\nu_2 - \nu_1$, the width of the line from α. Now Lord Rayleigh[10] set $I_2 \; I_1 = 0.95$ for the ratio of I_1 and I_2 at which fringes vanish. This makes $\alpha = {}^1\!/_{40}$. Fabry and Buisson[11] took this quantity as ${}^1\!/_{16}$ in their measurements. This choice, it is seen, introduces a somewhat arbitrary interpretation of the measurements. Of course, this factor varies with individual observers and the judgment as to the value for vanishing could be tested by an artificial study of visibility with known values of I_1 and I_2, which was actually done by both investigators.

Since ν, the changed frequency of light of an original frequency ν_0, obtained by superposing on the source a velocity u, is by the Doppler principle given by $\nu = \nu_0\left(1 + \frac{u}{V}\right)$, and since the values of u imposed on the molecules in a glow-discharge tube are given by Maxwell's distribution law, it is possible to compute the value of δ for which the fringes would disappear (*i.e.*, for which $\alpha = {}^1\!/_{40}$ or ${}^1\!/_{16}$, depending on who made the measurements). Here V is the velocity of light. This can be carried out for the case where the molecules have a uniform velocity u and for that where the velocity distribution is Maxwellian, of average value u. If one chooses a parameter $p = \frac{\delta}{\lambda_0} = \frac{\delta\nu_0}{V}$, this limiting order of interference p (the number of waves in the path difference δ for which the interference fringes disappear) is given by

$$p = 1.03 \times 10^6 \sqrt{\frac{M}{T}}$$

for a uniform velocity, and

$$p = 1.42 \times 10^6 \sqrt{\frac{M}{T}}$$

for a Maxwellian distribution, using the Rayleigh value for α.

If the Fabry and Buisson[11] value of α is used, the limiting order of interference becomes

$$p = 1.22 \times 10^6 \sqrt{\frac{M}{T}}$$

in the Maxwellian case, the subjective criterion for disappearance corresponding to that value of α. In all these equations M is the molecular or atomic weight and T is the absolute temperature. Thus, in the Rayleigh case the evidence for the existence or non-existence of the Maxwellian distribution depends on a variation of a constant numerical factor in the limiting order of interference, $p = \delta\nu_0/V$, of the order of 40 per cent. It is evident that the presence or absence of *a distribution of velocities* would be clearly demonstrated by the value of p. However, only a small divergence of p from the value computed, which could be well within the limits of experimental error, might indicate a serious departure from the Maxwellian distribution law.

The actual measurement of p was first made by Michelson and seemed to bear out the theory fairly well. The later results of Fabry and Buisson, however, seem to give an even more satisfactory agreement. The light from Geissler discharge tubes which were immersed in thermostated baths to keep T constant was analyzed by means of an interferometer. The difference of path of the interfering rays was then increased until the interference fringes ceased to be visible. This gave δ. The gases used were the inert gases, such as He, Ne, and Kr, as well as some ordinary gases like H_2. Under the conditions of the experiment the frequencies used came from lines known to have only a simple structure—that is, no complicated lines were chosen. Such lines come from the atoms of the elements, as is well known, for molecules give broad bands. Further experiments were made with the Geissler tubes immersed in liquid air to gain another value for T. M was given by the atomic weight of the gas. The value of p obtained from the value of δ at which interference fringes disappeared by dividing by λ_0 is given in column 4 of the table following. The calculated value of p from the values of M and T for the gases are given in the fifth column for room temperatures. For liquid-air temperatures the values

Gas	Atomic weight	Wave length A°	Room temperature		Liquid-air temperature	$\frac{p'}{p}$
			p obs.	p calc.	p' obs.	
He.....	4	5,876	144,000	144,000	241,000	1.66
Ne.....	20	5,852	324,000	321,000	515,000	1.60
Kr.....	83	5,570	600,000	597,000	950,000	1.58

of p' observed are given in the sixth column. The ratio of the value of p' observed at the liquid-air temperature to that at room temperature is given in the seventh column. The theoretical value for this, *e.g.*, $\sqrt{T/T'}$, is 1.73. Thus it seems as if the discharge warmed the gas slightly above the temperature of the bath.

The results show definitely the following facts: First, that p varies experimentally quite accurately as $\sqrt{M}$. Second, that it varies as $\sqrt{1/T}$ as accurately as the temperature conditions can be verified. Finally, p in order of magnitude agrees very well with the value computed from Maxwell's law. However, this agreement, which is within 1 per cent, is rather forced through the choice of $\alpha = 1/16$. For $\alpha = 1/40$, as suggested by Lord Rayleigh, the value would be about 14 per cent higher. Thus a complete verification of the law which depends on an accurate agreement between the constants can hardly be said to have been achieved. The much more certain proof of the law would result from a photometric comparison of the intensity of the fringes, *i.e.*, of J_2/J_1 and hence of α at different values of δ. This would give a complete and accurate verification of the law. It may again, however, be added that this work does definitely prove the existence not only of molecular velocities but of a distribution of velocities.

For a discussion of the proof of the distribution law to be obtained from effusion the reader is referred to Secs. 41 and 79. The proof while indicating a distribution of velocities is not very rigorous as the constant factor varies little with the law.

46. The Direct Measurement of Molecular Velocities.—The direct and what will be the most complete and accurate verification of the distribution of velocities is the result of the development of the technique of molecular beams or rays. This relatively new development began with investigations of Dunnoyer,[47] incident to the improvements in vacuum technique in 1911. Using the straight-line free paths of molecules or atoms issuing from narrow slits in reservoirs at relatively low gaseous pressures into high vacua, and further defining the issuing jet by additional slits, beams or rays of molecules moving parallel to each other with rare collisions can be achieved. Such beams are ideal for the experimental study of many phenomena such as the measurement of molecular velocities, distribution of

free paths, magnetic and electrical moments of single atoms or molecules, problems of condensation and reflection from surfaces, and finally the diffraction of matter waves. A very fine elementary treatment of this whole subject is given in Fraser's book, "Molecular Rays."

It was Otto Stern,[5] perhaps the leading experimentalist in this field, who in 1920 showed the way by making the first direct measurements of molecular velocities. The method used was exceedingly simple. A platinum wire W on the axis of a rotating system (Fig. 24) was heavily coated with silver in such fashion that when heated it emitted a stream of silver atoms in a high vacuum. Around the filament W as axis, there was rotated at high speed a rigid system consisting of a narrow slit S, parallel to W, and a plate P opposite the slit. The filament which gave a line source of atoms with the rotating defining

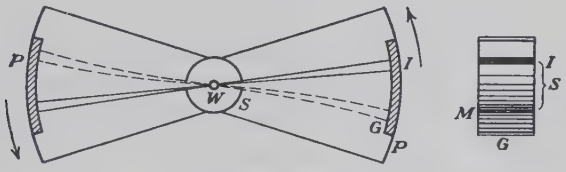

FIG. 24.

slit some 3 mm away thus produced a sharp narrowly defined beam of silver atoms. If the system SP was at rest, this beam was caught on the plate P, distant some 6 cm from the filament and gave a line image I of the filament. When the slit S and plate P were rotated, the molecules in the beam from the filament to the slit, which succeeded in getting through the slit, started on their path toward the plate. In the finite time taken for them to cross the 6 cm from the slit to the plate, the plate rotated through a finite angle. If the molecules were all of the same velocity, one would expect the image of the slit, due to the deposit of silver atoms on the moving plate, to be displaced a finite distance in a direction contrary to the direction of motion of the plate. The amount of the displacement must depend on the distance of the filament from the plate, the molecular velocity, and the speed of rotation. Call L the distance of W from P and the molecular velocity v, then the time to go from the filament to the plate is $\tau = L/v$. If the frequency of the rotation of the plate is ν, the plate moves $2\pi\nu L\tau$ cm while the atoms go from

W to P. Thus the image of the slit will for a line image be displaced $S = \frac{2\pi L^2 \nu}{v}$ cm from the image obtained at rest, in a sense contrary to the direction of rotation. Hence, by measuring S, L, and ν, the value of v can be determined. Actually the problem is complicated because the slits have finite width and by the fact that the atoms have a distribution of velocities. If the slits were infinitely narrow, then, what was a line for the system at rest would not only be displaced contrary to the rotation but would also be spread out into a *series of images of the slit for each velocity present.* In other words, the image with the rotating system would be drawn out into a velocity spectrum M. By a photometering of the deposit of the silver on a glass slide G fixed to the moving plate, the position of the image at rest and the distribution law due to the distribution of the density of the deposit for the moving system can be obtained. Corrections must be made for the axial finite length of the filament and for the finite width of the slit, which slightly complicates the observed distribution law. Stern, at 2,700 r.p.m., observed a deflection of the beam of 1.2 mm. From the deflection he calculated the value of C_1 for the molecules of silver evaporating to be 675 meters per second. The temperature of the filament used was about 1200°C., which corresponds to a value for C_1, which on theory is $\frac{4RT}{M}$, of 672 meters per second. The resolution was, however, not great enough to verify the shape of the distribution curve.

In writing the first edition of this text[48] the author was impressed with the necessity of a more complete verification of the distribution law and stated that he believed an extension of the Stern method could give much more perfect results. At his suggestion a modification of the Stern method with very high resolving power was designed by Prof. E. E. Hall and built by N. Herod under Hall's direction in 1927. Through the able technique of I. F. Zartman[44] the possibilities of the method were experimentally realized in 1930. Finally C. C. Ko,[45] with great perseverance and skill, overcame the remaining inaccuracies and was able to achieve a really satisfactory verification the results of which will be given later.

At the same time, about 1926, Costa, Smyth, and Compton,[42] and also Eldridge[43] in America, and independently and perhaps

before them, O. Stern[49] in Germany, devised a different method for accomplishing the same end. This method utilized the principle of the toothed wheel originally used by Fizeau for measuring the velocity of light. This method was finally brought to a sufficient perfection by Lammert[41] to enable a quantitative verification of the law to be achieved in 1929. In this method, atoms of Hg from a source and slit system, S_1, S_2 (Fig. 25) fall on to the slots in a rapidly rotating disc D_1. On the same shaft as this disc and 6 cm distant was a second disc D_2 with an inner row of slots, displaced 2 deg. relative to the slots in the first. In line with the first slit system and the slots in the discs but

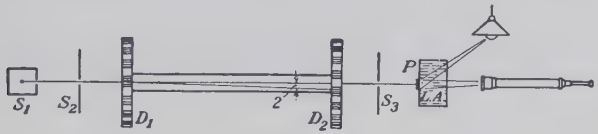

FIG. 25.

beyond the second disc was a slit S_3 backed by a fixed plate of glass, cooled with liquid air LA, which could be observed from the outside. With an outer set of slits on D_2 that were not displaced lined up and everything in position, the advent and condensation of the Hg atoms on the glass could be observed. By timing the appearance of a visible deposit, the intensity of the beam could be measured. Careful control experiments had shown that the appearance of a visible deposit always represented the arrival of the same number of atoms per cm^2, and, since the density of deposit depends on the product intensity of the beam times time, an observation of the time of appearance gave the intensity of the beam as long as the source was operating under constant conditions. If the discs were set in rotation, the molecules entering at any slit passed through the inner slits in the second disc only if during the time of transit of the molecules with a given velocity the discs had turned through angles such that the first, the second, third, fourth, etc., slit of the farther wheel was opposite the receiving slit. Had only one velocity been present, then there would have been deposits occurring in a minimum of time only when the speed of rotation was adjusted so that the first, second, third, fourth, etc., receiving slit was opposite the receiver when the molecules arrived.

With a distribution of velocities present, the arrival of the very fast molecules is registered for a speed just less than that

cutting off all molecules. By gradually decreasing the speed the various slower groups get through, and for still slower speeds, just before cut-off, the very slow molecules get through. This renders it difficult to obtain the fastest and slowest molecules as the appearance of the very fast molecules from the second slit begins to overlap the slowest molecules from the first. A greater range of velocities can be observed by using small slits and large distances between them, which reduces the beam intensity to impossible values. By properly adjusting the speeds used, bands of velocities between certain limiting values can be passed through due to the finite width of the slits. For each band the time of appearance of the deposit on the receiving plate corrected for the drop in intensity due to the teeth of the wheel was noted so that an estimate of the relative number of

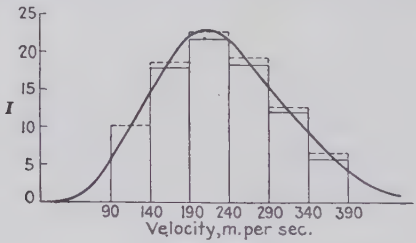

FIG. 26.

molecules in each limited velocity group was obtained. In this fashion, using 50 slots and from 12.1 to 40 revolutions per second velocity, bands differing by 50 m/sec. were separated out and their intensity was measured. The intensities of these bands plotted against the velocities observed are drawn in Fig. 26. It is seen that the curve drawn through the mid-points of these groups gives a fairly satisfactory Maxwellian curve. The use of the device by Stern and his school for obtaining more or less monochromatic velocity beams of molecules in later years is exemplified in the beautiful diffraction experiments of the De Broglie waves for He and H_2.

A very recent and accurate verification of the distribution law has been published by Meissner and Scheffers.[46] In this case a beam of potassium or lithium atoms was passed through an inhomogeneous magnetic field perpendicular to the path of the beam. The experiment was essentially to be a very accurate repetition of the early Stern-Gerlach measurement of magnetic

moments which is described in Sec. 103. This beam of potassium or lithium atoms, due to the magnetic moment of the atom, is divided by the field into two types of atoms, those having their magnetic axes parallel and those having their magnetic axes antiparallel (at 180 deg.) to the field (see page 539). In such a field those atoms with parallel moments are attracted to the one pole while the others are repelled from that pole by the divergent field. The magnetic force is constant so that a beam of atoms from a slit perpendicular to the axis of the field will be deflected toward or away from the position in the absence of the field by an amount dependent on the gradient of the magnetic field $\delta H/\delta Z$, the magnetic moment μ of the atom, and the time t which the atom is in the magnetic field, according to an equation $S = \frac{1}{2}at^2$, where $a = \frac{\mu}{m}\frac{\delta H}{\delta Z}$. This time t is merely the time taken for a molecule of velocity c to traverse the distance l in the field along the face of the pole pieces. Hence, since c which is determined by the Maxwellian distribution, varies, the value of $t = \frac{l}{c}$ will vary and S_c will be given by $S_c = \frac{1}{2}\frac{\mu}{m}\frac{\delta H}{\delta Z}\frac{l^2}{c^2}$.

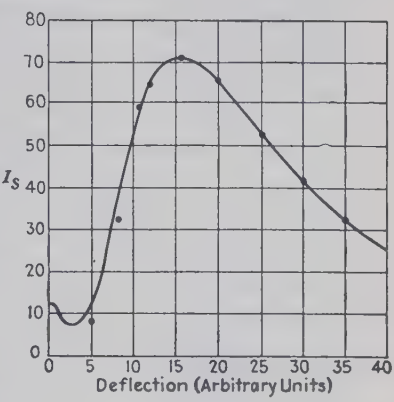

FIG. 27.

For a finite width of slit, of course, corrections must be made. Hence the deflected beams will be spread out in intensity according to a Maxwellian distribution curve for molecules emitted with a velocity c to the right and left of the central image, in the absence of a field. The method of detection was to use a fine slit in a small chamber parallel to the original beam. In this chamber was a fine incandescent platinum or other wire parallel to the slit. It now happens that atoms of the alkali metals, on striking such a filament, are reemitted as ions. By measuring the positive ion current from the filament as the small chamber is moved by micrometer screw across the beam, the relative intensities of the beam at different displacements S_c are at once determined. The result for Li is shown in Fig. 27 for the right-hand deflection of the beam. The line is the

observed curve, the points are the calculated points assuming μ to be one Bohr magneton (see Sec. 101). The rise at the center is due to a few *molecules* of Li, Li_2 which are present in the vapor and are non-magnetic ($\mu = 0$) and hence are not deflected. It is seen that, except near the very high velocity region near the center, the distribution law is close to that calculated from Maxwell's law. The deviation there may be due to the presence of the Li_2 molecules. This agreement confirms the value of the Bohr magneton as well as the Maxwell law to an asserted accuracy of 0.5 of 1 per cent.

The modification of the Stern method, developed at the University of California,[44,45] is as follows: As shown in Fig. 28, the atoms or molecules emerge from an oven O heated by radiation from a filament F. The beam is then produced by the slits S_1 and S_2 in the highly evacuated space. The rapidly spinning cylinder C is rotated at about 6,000 r.p.m. or more by a high-speed motor housed in the same casing about an axis A. It has a slit S_3 on one side and opposite, on the other side of the cylinder, a clamp made for holding the glass plate G so that it can always be replaced in its former position after removal. The plate is bent to the curvature of the flange of the disc and coated with a thin uniform deposit of the metal to be used, *e.g.*, Bi. Then it is placed in position in the cylinder and the chamber evacuated. The furnace is heated and at a given time the slide B at S_2 is opened, permitting the beam to strike the plate at the forward (right-hand edge) for a sufficient time to give a good deposit. This occurs when the cylinder is at rest and O, S_1, S_2, S_3 are all in line. The plate is removed and photometered on a recording microphotometer. It is then replaced, the chamber sealed and evacuated, the motor set into motion in a clockwise sense, and allowed to steady down. The slide B is again opened and a run of some 10 hr. is made in order to obtain a deposit of sufficient thickness on the plate. The plate is then removed and again photometered. The

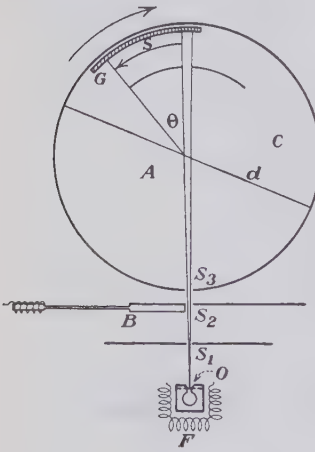

FIG. 28.

differences between the ordinates of the initial deposit with fixed disc and those of the curves with the revolving disc on the two microphotometer plates are then measured. A picture of the two microphotometer curves superposed is shown in Fig. 29

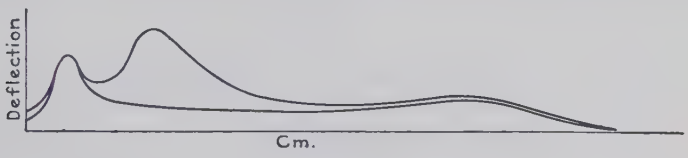

FIG. 29.

for Bi. In Ko's apparatus the rotation of the disc was *counter*-clockwise so that the zero image and fast molecules are to the left and the slow molecules are to the right in Figs. 29 and 30, *i.e.*, the reverse of what they would be if the schematic revolution of Fig. 28 had been used. Correction for the absorption curve of the deposit then enables one to plot the distribution curve

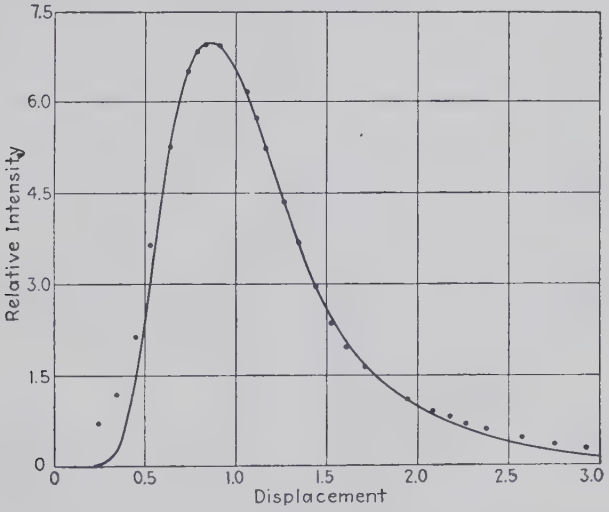

FIG. 30

for the substance. The distribution-law curve, assuming Maxwell's law, the temperature of the oven, and speed of rotation with correction for slit width, is then computed. The full-computed curve and the observed experimental points are compared in Fig. 30. As is seen, the agreement is good. Complete agreement is prevented, due to diffuse molecules, to the gradual change of slit width due to the accumulation of Bi at S_2, and due to the presence of Bi_8 molecules in the beam.

It can be seen from the foregoing that the Maxwell distribution law has been established directly, with a considerable degree of success by several different methods.

References

1. Jaeger, G.: Winkelmann's "Handbuch der Physik," 2d ed., vol. 3 (Wärme), p. 697, Johann Ambrosius Barth, Leipzig, 1906.
2. Meyer, O. E.: "Kinetic Theory of Gases," translated and revised by Robert E. Baynes, Chap. IV and Appendix III, Sec. 30, p. 415, Longmans, Green & Co., London, 1899.
3. Jeans, J. H.: "Dynamical Theory of Gases," Appendix B, p. 436, for Tables of $\psi(x)$, Cambridge University Press, Cambridge, 1921. See also Appendix of this book. (Dover Reprint)
4. Langmuir, I.: *Phys. Rev.*, **2**, 329, 1913.
5. *a.* Stern, O.: *Z. Physik*, **2**, 49, 1920; **3**, 417, 1920; *Phys. Z.*, **21**, 582, 1920.
   b. Gerlach, W.: "Ergebnisse der Exakten Naturwissenschaften," vol. 3, p. 182, Julius Springer, Berlin, 1924.
6. Richardson, O. W.: "Emission of Electricity from Hot Bodies," Longmans, Green & Co., London, 1921.
7. Bloch, E.: "Kinetic Theory of Gases," Chap. X, translated by P. A. Smith, Methuen, London, 1924.
8. Baly, E. C. C.: "Spectroscopy," Chaps. IX, XV.
9. Michelson: *Phil. Mag.*, **13**, 236, 1882; **34**, 280, 1892; **31**, 338, 1891; *Astrophys. J.*, **3**, 251, 1896.
10. Rayleigh: *Phil. Mag.*, **27**, 298, 1889.
11. Buisson and Fabry: *J. Phys.*, **2**, 442, 1912.
12. Rayleigh: *Phil. Mag.*, **29**, 274, 1915.
13. Richardson, O. W.: *Loc. cit.*, Chap. II.
14. Riecke, E.: Marx's "Handbuch der Radiologie," vol. 6, "Electron Theory of Galvanic Properties of Metals," Chap. I, p. 281; Chap. II, p. 302; Akademische Verlagsgesellschaft, Leipzig, 1924.
15. Schottky: *Ann. Physik*, **44**, 1011, 1914.
16. Jones: *Proc. Roy. Soc.*, **A102**, 734, 1923.
17. Germer: *Phys. Rev.*, **25**, 795, 1925.
18. Boltzmann, L.: "Vorlesungen über die Gas Theorie," Chap. I, p. 15, Johann Ambrosius Barth, Leipzig, 1910.
19. Clemens-Schaefer: "Einführung in die Theoretische Physik," vol. 2, part I, Sec. 30, pp. 81, especially 89, 90, 91, 92, 339; Vereinigung Wissenschaftlichen Verleger, Berlin, 1923.
20. Clemens-Schaefer: *Loc. cit.*, vol. 2, part I, pp. 401 and 403; Chap. X, p. 418, and especially pp. 450, 458ff.
21. Jeans, J. H.: "Dynamical Theory of Gases," Chaps. III, IV, V, Cambridge University Press, Cambridge, 1921. (Dover Reprint)
22. Ehrenfest, P. and T.: "Mathematische Encyklopädie," vol. 4 I; "Encyclopédie des Sciences Mathématiques," vol. 4, I, Paris, 1915. Gibbs, J. W.: "Elementary Principles of Statistical Mechanics," New York, 1902.

23. Waterston, J. C.: *Phil. Trans. Roy. Soc.*, **183**, 1, 1845.
24. Maxwell, J. C.: *Phil. Mag.*, January and July, 1860; or "Collected Works," vol. 1, p. 378.
25. Boltzmann, L.: *Sitzb. Akad. Wiss. Wien*, p. 58, 1861.
26. Maxwell, J. C.: *Phil. Mag.*, p. 21, 1879; or "Collected Works," vol. 2, p. 713.
27. See Chap. IX, Secs. 91, 92, 93, 94.
28. See Chap. IX, Secs. 91, 92.
29. Boltzmann, L.: *Loc. cit.*, vol. 1, p. 15.
30. Lorentz, H. A. *Sitzb. Akad. Wiss. Wien*, **25**, 115, 1887.
31. Jaeger, G.: "Handbuch der Physik," Geiger und Scheel, vol. 9, Secs. 26–28, pp. 369ff., Julius Springer, Berlin, 1926.
32. Jaeger, G.: *Loc. cit.*, Secs. 31–37, inclusive.
33. Jaeger, G.: *Loc. cit.*, Sec. 47, p. 396ff.
34. Jaeger, G.: *Loc. cit.*, Sec. 36, p. 380.
35. Jaeger, G.: *Loc. cit.*, Sec. 25, p. 368.
36. Weisskopf, V.: *Phys. Z.*, **34**, 1, 1933.
37. Knudsen, M.: *Ann. Physik*, **28**, 999, 1909.
38. Sommerfeld, A.: *Z. Physik*, **47**, 1, 1928.
39. Darrow, K. K.: *Rev. Mod. Phys.*, **1**, 90, 1929.
40. Dushman, S.: *Rev. Mod. Phys.*, **2**, 381, 1930.
41. Lammert: *Z. Physik*, **56**, 244, 1929.
42. Costa, Smyth, and Compton: *Phys. Rev.*, **30**, 349, 1927.
43. Eldridge, J. A.: *Phys. Rev.*, **30**, 391, 1927.
44. Zartman, I. F.: *Phys. Rev.*, **37**, 383, 1931.
45. Ko, C. C.: *Jour. Franklin Inst.*, **217**, 173, 1934.
46. Meissner and Scheffers: *Phys. Z.*, **34**, 48, 1933.
47. Dunnoyer, "Popular Lectures," Société Française de Physique, sér. 2, p. 214, Gauthier Villars, Paris, 1913.
48. Loeb: "Kinetic Theory of Gases," 1st ed., p. 104.
49. Stern, O.: *Z. Physik*, **39**, 751, 1926.
50. Kammerlingh-Onnes: *Arch. Néerland*, **30**, 113, 1897.

Books Recommended

a. Winkelmann, A.: *Loc. cit.*
b. Meyer, O. E.: *Loc. cit.*, Chap. III, Appendix II.
c. Clemens-Schaefer: *Loc. cit.*
d. Bloch, E.: *Loc. cit.*
e. Richardson, O. W.: *Loc. cit.*
f. Gerlach, W.: *Loc. cit.*
g. Hertzfeld, K. F.: "Kinetische Theorie der Wärme," (Section of Müller-Pouillet's "Lehrbuch der Physik") Chap. Iα, Secs. 7–10 also Sec. 16 for simple discussion of distribution law and its proof. Chap. IIα, β, γ and especially $\gamma 8$ for elementary statistical mechanics. F. Vieweg und Sohn, Braunschweig, 1915.
h. Jaeger, G.: "Handbuch der Physik," Geiger und Scheel, vol. IX, Chap. VI, pp. 340–471, Julius Springer, Berlin, 1926.
i. Fraser, R. G. J.: "Molecular Rays." Cambridge University Press, Cambridge, 1931.

CHAPTER V

THE MORE ACCURATE EQUATION OF STATE, OR VAN DER WAALS' EQUATION

47 Introduction.—In the discussion of the gas laws on the basis of the kinetic theory, which has preceded this chapter, the molecules have for the most part been considered as points which have no forces acting between them. In the deduction of the expression for the mean free paths in Chap. III it became necessary to consider that the molecules have a volume, and use was made of a quantity b related to $\frac{4}{3}\pi r^3 N$, the total volume of the molecules present in a cm^3. In fact, the pressure of a gas as calculated by Clausius in Sec. 19 made an allowance for such a term. As was shown in the second chapter, the kinetic hypothesis leads to the expression $pv = RT = \frac{1}{3}\nu m C^2$ for the type of gases postulated. This is commonly known as the Boyle's-Charles' law, and it holds true for the "permanent" gases under the experimental conditions usually employed in the common laboratory courses in physics, within the precision obtainable in such experiments. Even Boyle in his first measurements, however, noted that it did not hold rigorously, and stated the fact. As will presently be seen, accurate experiments show that this law does not hold at all accurately over large ranges and with a higher precision of measurement. The departures from this law, in part foreshadowed by Clausius in his theoretical treatment of the pressure relation, lead Van der Waals to his now famous equation of state. The development of the latter equation and its application to the interpretation of gaseous behavior will constitute the body of this chapter.

It should further be pointed out that, in turn, the Van der Waals equation has its shortcomings. While in its present form it covers the general behavior of gases beyond the realms of Boyle's law satisfactorily for a large number of gases, it breaks down quite seriously when compared with still more accurate results. To replace it, various modifications or extensions have

been made to correct the errors introduced by the simplifying assumptions underlying it. Thus, while specifically Van der Waals' equation extends the Boyle's law equation by endowing molecules with volumes and forces, it assumes these volumes constant and the forces independent of the state of the gas. Actually, these conditions are not fulfilled and the extensions of the equation, some merely empirical in nature, attempt to correct this difficulty. They, in general, succeed in being of use for one set of phenomena involving the law, but none of them have the general applicability of the simpler equation. Necessarily, the better equations of this type reduce to the Van der Waals equation in the limit when the factors causing the deviations from the equation are reduced to vanishingly small quantities. Again, the Van der Waals equation itself reverts to the simple Boyle's-Charles' law when the molecular volumes and forces approach zero.

It is of interest to note in passing that the development of this law is a beautiful illustration of the progressive advance of physical science. First there is the discovery of a general regularity or law of nature through crude quantitative measurement. This is followed by a stimulating "explanation" in terms of a mechanical analogy. Then, as the result of more accurate measurements, what might be called second-order deviations come to light. Following these appears a brilliant *extension* of the mechanical theory to include the deviations. It is to be noted that such a change in the theory is not *revolutionary* in any sense. Nothing is upset and no errors have been made. The further investigation merely indicates the limitations of the fundamental assumptions. Such limitations being discovered, a further extension is possible, and the accuracy of the theory is extended perhaps to another significant figure. Following this improvement still more precise measurement again reveals deficiencies which require extension of the theory. Thus the knowledge and comprehension of the phenomenon can continue indefinitely, new improvements in technique making further experiment possible, new extensions in mathematical treatment also making perfection of the theory possible. It might seem as if this process could go on *ad infinitum*. Unfortunately, as accuracy advances progress becomes increasingly difficult, owing to the increase in mathematical complexity. Thus it soon becomes almost impossible to handle some of the resulting involved expressions. A simple example of this also appears in the practical application of the

equation of state. To this day most engineers are, for simplicity, forced to assume the Boyle's law equation, since the complications introduced by the more accurate Van der Waals equation already begin to increase the complexity of their calculations more than the increase in accuracy would warrant.

The Van der Waals equation, accordingly, besides furnishing an admirable second approximation to the true behavior of gases, can be of value in indicating the manner of advance of scientific thought. From what has preceded, it is seen that, while it has its limitations, it is perhaps the most serviceable equation, for, owing to its still considerable simplicity, it makes it possible to deduce the values of the constants involved (*e.g.*, the size of the molecules and the constant of attraction) to a first order of approximation. With the more accurate modifications the increasing complexity of the quantities renders such evaluations more difficult, and the loss of generality in application renders correlation between the constants of the equation obtained from a variety of phenomena impossible. Thus by its means, as will be seen in this chapter, the molecular constants a and b can be determined and can be found to agree from three apparently independent sets of data, to wit: (1) deviation from the gas laws, (2) critical constants, (3) the Joule-Thomson effect.

48. Deviations from Boyle's Law and the Deduction of Van der Waals' Equation.—If the product $pv = RT$ = constant is plotted as ordinates against p, the pressure, as abscissæ, the resulting curve should be a straight line parallel to the axis of abscissæ as long as Boyle's law holds. This is shown in curve 1, Fig. 31. There are, however, no gases for which this is true if the measurements are accurately made. For the gases H_2 and He the product pv plotted against p gives nearly a straight line, which rises gradually as p increases. The behavior for these gases is seen in curve 2, Fig. 31. For most gases, however, the curve for the product pv at first falls below pv equals a constant, as p increases, and later rises above this line. For O_2 and N_2 the decrease is slight, while for the more condensible gases the initial drop is more pronounced. Such a curve is shown in curve 3, Fig. 31.

The explanation of these phenomena is qualitatively simple. In the first place, if Clausius' deduction of the pressure relation which allows for the volume of the molecules is correct (Sec. 19), *i.e.*, if $p(v - b) = RT = \frac{1}{3} m\nu C^2$, then $pv - pb = RT$, or, better,

$pv = RT + pb$. Thus, as p increases pv *increases* linearly with it. Its rate of increase is then determined by b, the coefficient of p, and the greater b the more rapid the rise. This b is nothing but a function of the volume of the molecules, which was taken as four times the total volume of the molecules present in the volume v of the gas, so that it should be possible from such deviations to evaluate b and hence the size of the molecules. Thus the deviations of the type-2 curve is satisfactorily explained by taking account of the volumes of the molecules. The initial fall of the curves of the third type in Fig. 31, however, still requires explanation. This curve demands that, as p increases, the product pv must first decrease, that is, v must decrease *more*

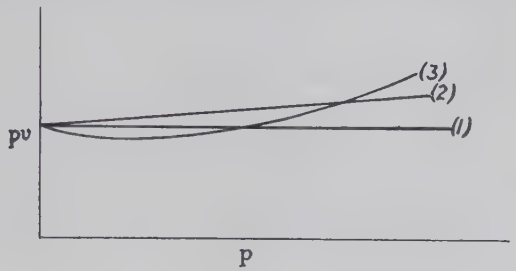

FIG. 31.

rapidly than p increases. Such a change in v can only take place if some pressure other than p is active in changing the volume. Now the fact that molecules condense to form a liquid or a solid under the proper conditions indicates very definitely that the molecules attract each other. Thus the forceless molecules previously assumed must for all gases be replaced by molecules which attract each other. If this be assumed to be the case, and if it be further assumed that the attractive forces of the molecules extend over limited distances only, then the more molecules there are in a given volume the greater will be the attraction. Hence it would be expected that, as the volume decreases, the internal pressure due to the attractions of the molecules would increase. Thus it is to be expected from the behavior of the pv-p curves that, besides the external pressure p on a gas, there is an internal pressure p' due to mutual attraction of the molecules. This pressure p' is a function of the volume of the gas and must be added to p in any correct gas-law equation.

Van der Waals, in 1873, had the insight to derive an expression for the value of this pressure p' and thus to deduce an equation of

state which stands today as the most *generally* satisfactory approximation to the gaseous behavior. His evaluation of the pressure p' was based on an analogy to Laplace's famous equation of surface tension. Surface tension is again a phenomenon due to the mutual attraction of molecules, and hence it is not surprising that the type of reasoning successful in one case should be equally successful in a similar case. If one considers the outer layer of gas in a containing vessel, one notes first the external pressure p on this layer exerted by the walls. If, however, the gas molecules attract each other, those on the outside will not be attracted outward, as there is no gas present to attract them. They will, however, suffer an attraction inward by all inward lying molecules. Now it is obvious that the attractive forces of molecules on other molecules must vary with the distance. Hence it is conceivable that molecules lying far away from a given molecule will suffer negligible attraction from it. It must, accordingly, be assumed that, in general, there is a distance x in a gas beyond which the attraction of one molecule for another is negligible. What the magnitude of this distance is is not of material importance for the present discussion. Possibly it is of the order of a mean free path at N.T.P. One can, therefore, consider a layer of gas x cm thick, over the outer surface of the gas, in which each molecule has an inward component of force exerted on it by the molecules lying within x cm interior to it, for the inward components of force on these molecules are not balanced by outward components of force, since there are no molecules more than x cm outside of this layer to attract them.

Since the pressure on the layer is due to the molecules, it must be proportional to the number of molecules ν per unit volume in the outer layer. It must also be proportional to the number of molecules ν' per unit volume in the body of the gas attracting the outer layer. Thus the pressure is proportional to the product of the concentrations $\nu\nu'$ in the two attracting parts of the gas considered. In a gas in equilibrium, $\nu = \nu'$ so that $p' \propto \nu^2$.* For a given number of molecules, n, in the gas, $\nu = n/v$, where v is the volume of the space with n molecules. If n is constant, ν is proportional to $1/v$. Hence the pressure $p' \propto 1/v^2$ and one may write $p' = a/v^2$ where a is a constant. It is to be noted

* This at the outer surface is not strictly true but is legitimate in this discussion. The question is more fully discussed on p. 146.

that nothing was said concerning the laws of force assumed to exist, except that the force decreased so rapidly with the distance that the forces were negligible at distances of the order of the dimensions of the vessel. Experiment has shown that the shape of the vessel has no effect on the pressure p'. This fact can be shown to preclude laws of force that decrease as slowly or more slowly with the distance than $f \propto 1/r^4$. Hence the attractive forces must fall off as rapidly as $f \propto 1/r^m$, where m is equal to 5 or more. Again, when p' is written as equal to a/v^2, the quantity a taken as a constant of proportionality is so taken with a disregard of the fact that the *concentration* v *must be influenced by the attractive forces.* A consideration of this omission has the effect of making a a function of temperature as will be seen later. For the present, a may be assumed to be essentially constant. It is obvious that a must be a constant characterizing the attractive forces for each particular kind of gas and should be independent of the volume v of the gas. Thus the equation properly describing the behavior of a gas must contain the correction both for the volume of the molecules and for the value of the internal pressure. Thus Van der Waals' equation may be written

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT = \frac{1}{3}nmC^2.*$$

It is this equation which, in general, most conveniently fits the behavior of a gas to a second degree of approximation. By its application to gaseous behavior the values of a and b may be found for different gases.

Thus in the explanation of the curves of type 3 of Fig. 31, which was discussed, the equation takes the form

$$pv = RT + pb - \frac{a}{v} + \frac{ab}{v^2}.$$

Since a and b are both small ab/v^2 is a small quantity of higher order and may be neglected. Hence the expression for the quantity pv becomes $pv = RT + pb - a/v$. This equation very satisfactorily explains the initial drop of the pv curve as p increases. For if a is greater than b, as v decreases the a/v term increases

* The n here used represents the molecules in the volume v. It will hereafter be used in place of the ν formerly used.

more rapidly than pb increases. It seems as if the resulting decrease of pv should go on indefinitely. As the pressure goes still higher, however, the volume becomes so small that the molecules become crowded together and the spaces between them become of the same order of magnitude as the molecules themselves. When this point is reached, further changes in p produce comparatively small changes in v (*i.e.*, $1/v$ is no longer proportional to p). Thus the pb term increases more rapidly than the a/v term and soon becomes the important factor causing the curve to rise again. With H_2 and He, however, the a is so small as to cause little or no change in the slope of the curve due to pb, and the type-2 curves result. Hence one may already qualitatively see the differences in gaseous behavior due to a difference in the constant a.

The expression for the internal pressure of the gas due to attractive forces may be deduced rigorously from the attractive forces. The deduction will follow one due to R. H. Fowler[11] as this procedure gives a far better insight into the nature of the Van der Waals a.

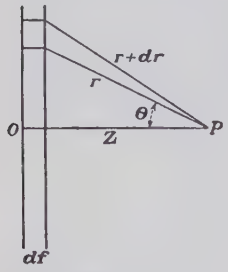

FIG. 32.

Consider an infinite plane slab of gas of thickness df shown in Fig. 32, and calculate the average force dF exerted by all the molecules in df on a molecule at a point P distant Z cm from the slab. As collisions do not enter, one may regard the molecules as point centers of force. Assume n molecules in a volume v of the gas. Then in unit area of df there are $\frac{n}{v}df$ molecules in the *absence* of the molecule at P. However, if a molecule is at P, the field of force at df due to the molecule at P will so *alter the distribution* that there will be a change in the number of molecules due to the force field. In Sec. 36 it was shown that the number of molecules finding themselves at a point in a force field where the potential energy was u, was given by

$$n_u = nAe^{-\frac{u}{kT}}d\tau.$$

In the present case, the number of molecules in the volume of unit area and df thick at a distance r from P will be $\frac{n}{v}dfe^{-u_r/kT}$,

where u_r is the potential energy due to the force field of the molecule at P and is a function of r.

To obtain the force on the whole slab, choose an annulus of width dr at a distance r from P and determine the force due to this annulus at P. This annulus contains $n_1 = 2\pi r \sin\theta \frac{dr}{\sin\theta} \frac{n}{v} df e^{-u_r/kT}$ molecules as seen from Fig. 32. The force on these molecules due to P is then $n_1 \frac{\delta u_r}{\delta r} \cos\theta$, for the resultant force must be along the normal PO of the slab. Inserting the value of n_1 in the equation and writing $r\cos\theta = Z$, one obtains the force as $2\pi \frac{n}{v} df Z \left(\frac{\delta u_r}{\delta r}\right) e^{-u_r/kT} dr$. The total force dF on the molecule at P due to the whole slab is obtained by canceling the differentials in r and integrating for all values of r from Z to infinity. This process gives dF as

$$dF = 2\pi \frac{n}{v} kTZ df (e^{-\frac{uz}{kT}} - 1).$$

In a slab of unit area of thickness dZ at P there are $\frac{n}{v} dZ$ molecules acting like the one at P. Thus the two slabs separated by a distance Z attract each other by a force per unit area in amount

$$2\pi \frac{n^2}{v^2} kTZ dZ df (e^{-\frac{uz}{kT}} - 1).$$

To determine the total pressure of the gas, the force per unit area between the two slabs must be integrated from 0 to ∞ over both df and dZ. The distance Z between the slabs df and dZ must be taken as $f + Z$. Then the pressure is given by

$$2\pi \frac{n^2}{v^2} kT \int_0^\infty \int_0^\infty (Z + f)(e^{-\frac{u(Z+f)}{kT}} - 1) dZ df.$$

Changing the origin for integration so that $(Z + f) = x$, and $df = dy$, the integral becomes

$$2\pi \frac{n^2}{v^2} kT \int_0^\infty x(e^{-\frac{ux}{kT}} - 1) dx \int_0^x dy = 2\pi \frac{n^2}{v^2} kT \int_0^\infty x^2 (e^{-\frac{ux}{kT}} - 1) dx.$$

This gives at once the force per unit area due to the attractions of the molecules on two sides of a bounding plane in the gas. If a sufficiently thick slab of gas be regarded between two

infinite parallel planes in the body of the gas, this gas mass will be in equilibrium due to the forces per unit area of equal magnitude but opposite directions across the two planes. If now the layer of gas above the upper boundary be removed, and if the section be of such thickness t that the force $\delta u_x/\delta x$ approaches 0 at distances of the order of t, the gas between the two planes exerts an unbalanced pressure p' on the interior layer. This pressure p' is just the Van der Waals internal pressure and is the force per unit area between thick gas layers whose value is

$$p' = 2\pi\frac{n^2}{v^2}kT\int_0^\infty x^2(e^{-\frac{u_x}{kT}} - 1)dx.$$

Hence, since $p' = a/v^2$, one has

$$a = 2\pi n^2 kT\int_0^\infty x^2(e^{-\frac{u_x}{kT}} - 1)dx.$$

There may be some question as to whether at a real gaseous boundary the pressure on the boundary layer is that arrived at above, owing to the fact that due to the variation of force with distance the distribution of molecules in the surface layer is not that ideally assumed above. Fowler[20] has shown, however, that the pressure p' can be calculated from the work done in carrying a molecule through the surface, taking into account the change of density at the surface. The result of this calculation turns out to be the same as that given above, so that there is no question of the accuracy of the result.

It is seen that the value of p' and hence a differs from that given by the elementary theory in that a is much more specifically evaluated and that a here is a function of T. Were the force function and hence u_x known as a function of distance x, the exact value of a could be determined in terms of T. That a is really not a constant as assumed by elementary theory but depends on T is here theoretically justified and is in agreement with experimental fact. As regards the function u_x it is interesting to note that the function probably varies as an inverse power of x, *i.e.*, $u_x \propto 1/x^m$, and that the exponent m must be greater than 4 in order that the a be independent of the size and shape of the vessel, an experimental observation.

49. Note on the Value of Van der Waals' b.—As has been stated in several places, b is a correction term in the pressure equation for the finite volume of the molecules present. At

first sight it might appear to be the total unavailable space for molecular motion, *i.e.*, the total *volume of the spheres of exclusion* of the molecules,

$$\frac{4}{3}\pi\sigma^3 N \text{ or } 8\left(\frac{4}{3}\pi r^3 N\right),$$

where $r = \sigma/2$. This was shown in Sec. 18 to be incorrect, as in any collision *only that hemisphere of the volume of exclusion is involved whose base is perpendicular to the direction of motion,* so that

$$b = \frac{1}{2}\left(\frac{4}{3}\pi\sigma^3 N\right) = \frac{2}{3}\pi\sigma^3 N = 4\left(\frac{4}{3}\pi r^3 N\right) = 4\omega.$$

This can be more rigorously deduced as follows. In a gas at pressures around that of the atmosphere the chance of collision between molecules is some tens of thousands of times more probable than with the walls of the containing vessel as shown in Sec. 15. Thus one regards the potential impacts as taking place with the irregular surface of the spheres of exclusion surrounding the molecule whose collisions are being studied. Owing to the finite volume of the spheres of exclusion, the volume available for the motion of the molecule in question is not a volume V described by the highly irregular surface made by joining the *centers* of all the surrounding molecules. It is instead a volume described by the *hemispherical surfaces of all the spheres of exclusion of the molecules* delimiting the available volume V, and *facing* the molecule in question, since this volume is denied to the single molecular center in question in its motion. This reduces the available volume V by a quantity $b = \frac{1}{2}\left(\frac{4}{3}\pi n_1\sigma^3\right)$, where n_1 is the number of molecules delimiting the volume V. Thus the volume available is $V - b$. Hence the volume available for motion in the usual cases considered is $V - b$, where $b = 4\omega$.

In classical kinetic theory, many attempts have been made to compute this volume b, utilizing the shortening of the mean free paths of molecules due to the effect of collisions between molecules of finite volume having definite spheres of exclusion.[1,2,3,4,5] While this method furnishes a useful tool, it is strictly not relevant as the correction occurs at equilibrium, irrespective of the existence of mean free paths. In the attempt

to deduce a proper value of b, a number of erroneous deductions have crept into the classical literature of the past, which were treated at length in the first edition. Suffice it to say that an early faulty deduction of Van der Waals based on free-path considerations, gave the proper value of b. A later deduction of Van der Waals[1] corrected the blunder and obtained a different value. By including the distribution of velocities in the derivation, a factor neglected in earlier work, Van der Waals found that the correct deduction again gave the value of $b = 4\omega$ initially erroneously deduced. In view of the fact that the more accurate deductions of the equation of state from the theorem of the virial yield the same value of $b = 4\omega$, obtained above, a further consideration of the subject is superfluous. The value of b may thus safely be taken as $b = \frac{1}{2}\left(\frac{4}{3}\pi\sigma^3 N\right)$ and will so be used hereafter. It should again be noted that in all these deductions, the molecules are taken as solid elastic spheres of radius r and diameter σ. Actually, as will be shown later, this is not the case. The quantity σ is determined by the repulsive forces due to the interaction of repulsive interatomic force fields of the form $f_1 = -a_1/r^n$, reduced in value by the superposition of attractive force fields $f_2 = +a_2/r^m$, where n ranges between 9 and 14 while m is of the order of 5 or 6. The resultant increase of repulsive force $f_1 - f_2$ causes the forces of repulsion to become so large with small changes in r that the molecule *acts* much as a hard elastic sphere of radius $\sigma/2 = r_1$, not much less than r_0, the value of r at which $f_1 = f_2$. For violent impacts the centers of the molecules will approach to less than r_0 and to smaller distances the more violent the impacts. Thus $r_1 = \sigma/2$ is a very slowly changing function of temperature. It must further be noted that while the correction for the volume of the molecules, b, has the value deduced above for total available volumes V which are much greater than $2b$, when V becomes comparable with $2b$ or less, the correction to V for the volumes of the spheres of exclusion must take on a different value. Of the limitations imposed by this fact on the equation of state, much more will be said at another point.

It is thus again clear that the volume correction b is only approximate, that it may vary with the velocities of the molecules (temperature), and that it is only correct for values of V somewhat exceeding $2b$, below which b is a function of the volume V

and takes on a different value. At very low pressures and practical volumes the effect of molecular spheres of exclusion becomes entirely negligible in comparison with the volumes V available for motion.

50. Deduction of Van der Waals' Equation from the Theorem of the Virial.—A more rigorous and perhaps more satisfying deduction of Van der Waals' equation comes from a consideration of Clausius'[6] well-known theorem of the virial. As it is not readily accessible to the reader, it may not be out of place to discuss it at this point.

It is first necessary to deduce the theorem of the virial in order to understand its function. The derivation here used is taken from the admirable treatment of Clemens-Schaefer.[7] Let it be assumed that the equations of dynamics may be applied to the centers of gravity of each of the molecules of mass m of a homogeneous gas. Then one can write for the equations of motion of these molecules

$$m\frac{d^2x}{dt^2} = X,\ m\frac{d^2y}{dt^2} = Y,\ \text{and}\ m\frac{d^2z}{dt^2} = Z.$$

In these equations the coordinates of the molecule along the three axes are x, y, and z, while X, Y, and Z are the three components of the external forces acting on the molecule. Multiplying these equations through by x, y, and z, respectively,

$$mx\frac{d^2x}{dt^2} = Xx,\ my\frac{d^2y}{dt^2} = Yy,\ mz\frac{d^2z}{dt^2} = Zz.$$

Since, however, the quantity $mx\dfrac{d^2x}{dt^2}$ may be expressed by

$$mx\frac{d^2x}{dt^2} = \frac{d^2\left(\frac{m}{2}x^2\right)}{dt^2} - m\left(\frac{dx}{dt}\right)^2,$$

and similarly for the y- and z-components, these equations of motion may be written in the following fashion:

$$\frac{d^2\left(\frac{mx^2}{4}\right)}{dt^2} - \frac{m}{2}\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}Xx.$$

$$\frac{d^2\left(\frac{my^2}{4}\right)}{dt^2} - \frac{m}{2}\left(\frac{dy}{dt}\right)^2 = \frac{1}{2}Yy.$$

$$\frac{d^2\left(\frac{mz^2}{4}\right)}{dt^2} - \frac{m}{2}\left(\frac{dz}{dt}\right)^2 = \frac{1}{2}Zz.$$

Adding these quantities together,

$$\frac{m}{4}\frac{d^2}{dt^2}(x^2 + y^2 + z^2) - \frac{m}{2}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right] = \frac{1}{2}(Xx + Yy + Zz).$$

The equation applies to one molecule, and it must now be summed up for all molecules of the gas. Thus,

$$\frac{m}{4}\sum\frac{d^2}{dt^2}(x^2 + y^2 + z^2) - \frac{1}{2}\sum mc^2 = \frac{1}{2}\sum(Xx + Yy + Zz).$$

This equation can now be multiplied by an elementary time interval dt and integrated over a comparatively long time interval τ.*

$$\frac{m}{4}\sum\int_0^\tau\frac{d^2}{dt^2}(x^2 + y^2 + z^2)dt - \sum\int_0^\tau\frac{m}{2}c^2dt = \frac{1}{2}\sum\int_0^\tau(Xx + Yy + Zz)dt.$$

Dividing this quantity by τ,

$$\frac{m}{4\tau}\sum\left[\frac{d}{dt}(x^2 + y^2 + z^2)\right]_0^\tau - \frac{1}{\tau}\sum\int_0^\tau\frac{m}{2}c^2dt = \frac{1}{2\tau}\sum\int_0^\tau(Xx + Yy + Zz)dt.$$

If, now, the values of all velocities and coordinates are conceived of as remaining within finite limits, then for a relatively large τ the first term will become vanishingly small while the others remain finite, for the first term is divided by τ but contains no τ while the other terms contain τ as well as being divided by τ. The first term that does not vanish under the above conditions is nothing but the total kinetic energy of agitation of the molecules, averaged over a finite time. This may be written $\overline{\sum\frac{m}{2}c^2}^t$. The term on the right-hand side of the equation is the average

* This time interval need be long only in the sense of the average times between disturbances of the motion of a molecule. Since the mean free path is of the order of 10^{-5} cm and $\bar{c}$ is of the order of 10^4 cm/sec., the time for such an occurrence is 10^{-9} sec. Hence for the integration in question τ need not be a great fraction of a second.

value of the sum $\frac{1}{2}\sum(Xx + Yy + Zz)$, taken over a finite time interval, and it can be written as $\frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^{t}$. Now the quantity $\sum\overline{\frac{m}{2}c^2}^{t}$ is really nothing but the average total kinetic energy of the molecules present in a given volume, to wit $\frac{1}{2}nmC^2$, where n is the number of molecules present.

Then the equation becomes

$$\frac{1}{2}nmC^2 + \frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^{t} = 0.$$

The quantity $-\frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^{t}$ was called by Clausius the "virial" of the mechanical system; and the above equation states that the total kinetic energy of the system is equal to the virial of the same. This constitutes the famous theorem of the virial.

This theorem may at once be applied to deduce the expression for the equation of an ideal gas. Consider the gas enclosed in a parallelepiped of volume $V = abc$, the sides a, b, and c being parallel to the coordinate axes. For the ideal gas, no forces act between the molecules at all and merely the forces experienced by the molecules in impact with the walls need be regarded. Consider the two walls of the paralellepiped which lie parallel to the yz-plane, the one wall having the x coordinate equal to 0, the other wall the x coordinate equal to a. Now, denote the time average of the force on the wall per unit area by p. For the wall at $x = 0$, p is in the direction of the positive x-axis; for the wall at $x = a$, it is in the direction of the negative x-axis. Thus for the first-named wall $\sum\left(\overline{Xx}\right)^{t}_{x=0} = +pbc\ 0 = 0$, and for the second-named wall $\sum\left(\overline{Xx}\right)^{t}_{x=a} = -pbca = -pV$. Exactly the same value is obtained for each of the other two pairs of walls, whence $\frac{1}{2}\overline{\sum(Xx + Yy + Zz)}^{t} = \frac{3}{2}pV$. Thus the theorem of the virial at once gives $\frac{3}{2}pV = \frac{1}{2}nmC^2$, or $p = \frac{1}{3}\frac{nmC^2}{V} = \frac{1}{3}NmC^2$.

This is the simple equation for an ideal gas which was deduced in a very elementary fashion in Sec. 5.

It now becomes necessary to carry this deduction over to the case of the non-ideal gas. This treatment due to Reinganum is found in Jellinek and in Jaeger.[17] In this case intermolecular forces act on the gas molecules beside the forces assumed above, *i.e.*, those of the walls. These forces must be taken account of in the virial.

Let it be assumed that the molecules *are hard elastic spheres between which forces act which are functions of the distances between the molecules. Let it be further assumed that these forces decrease rapidly to* 0 when the distances between the molecules exceed a certain value. Call $\phi(r)$ the force between two molecules located at the points x, y, z, and x', y', z'. It then follows that r, the distance between them, is given by $r^2 = (x - x')^2 + (y - y')^2 + (z - z')^2$. The force components X, Y, Z and X', Y', Z' acting on these molecules are then given by the following relationships:

$$X = \phi(r)\frac{x - x'}{r} \qquad X' = \phi(r)\frac{x' - x}{r}$$

$$Y = \phi(r)\frac{y - y'}{r} \qquad Y' = \phi(r)\frac{y' - y}{r}$$

$$Z = \phi(r)\frac{z - z'}{r} \qquad Z' = \phi(r)\frac{z' - z}{r}$$

(*i.e.*, they are the projections of $\phi(r)$ on the X-, Y-, and Z-axes). The unaveraged virial for these two molecules thus becomes

$$-\frac{1}{2}\left[\left\{\phi(r)\frac{x - x'}{r}x - \phi(r)\frac{x - x'}{r}x'\right\} + \left\{\phi(r)\frac{y - y'}{r}y - \phi(r)\frac{y - y'}{r}y'\right\} + \left\{\phi(r)\frac{z - z'}{r}z - \phi(r)\frac{z - z'}{r}z'\right\}\right].$$

On rearranging these terms one arrives at the relation

$$-\frac{1}{2}\frac{\phi(r)}{r}[(x - x')^2 + (y - y')^2 + (z - z')^2] = -\frac{1}{2}r\phi(r).$$

One may then sum up the value for one pair of molecules over all the pairs of molecules and obtain the virial of the interatomic forces as simply $-\frac{1}{2}\sum r\phi(r)$. It is therefore clear that this virial must be taken into account in arriving at the correct expression for the whole virial in the case of a real gas. That is,

the appropriate terms of this form for interatomic forces must be added to the expression for the virial of an ideal gas. Thus the virial for the ideal gas,

$$\frac{3}{2}pV - \frac{1}{2}nmC^2 = 0,$$

must have terms of the form above added to the left-hand side, if applied to a real gas. In order to insert these terms correctly, a more careful consideration of the properties of the molecules of a real gas must first be undertaken.

As has clearly been intimated in the previous deductions of Van der Waals' equation, the molecules are assumed to have a finite diameter σ and at the same time to exert attractive forces falling off rapidly (as fast as $1/r^5$ or faster) with the distance. When one asserts that a molecule has a diameter σ, one merely states that in impact, when the centers approach within σ of each other, there are abruptly manifested repulsive forces of a high order falling off exceedingly rapidly with the distance (*i.e.*, repulsive forces of the type of $1/r^9$ to perhaps $1/r^{14}$). In an average impact the molecular centers, under such conditions, cannot approach much more closely than σ. This distance of approach will vary slightly with the energy of impact, but, owing to the high order of the exponent of r, the variation may in some cases be neglected and σ then taken as constant. Likewise, at distances greater than σ the repulsive forces fall off so rapidly that they can be neglected. Nevertheless, there are repulsive forces at distances of the order of σ which must be included in the virial. At distances greater than σ the attractive forces come into play relative to the repulsive forces. These again fall off rapidly with the distances but *extend with appreciable magnitude over distances much greater than do the repulsive forces.* These also require a term in the virial and both the repulsive and attractive terms must be added to the simple expression for the virial of an ideal gas to make it applicable to a real gas. Since these terms are both due to interatomic forces, both will have the same form as that deduced above, *i.e.*, $r\phi(r)$. However, $\phi(r)$ in the virial for the repulsive forces will be represented by $f(r)$, where $f(r)$ is of the form $1/r^n$, n lying between 9 and 14; while for the attractive forces $\phi(r)$ will be represented by $F(r)$, where $F(r)$ is of the form $1/r^m$, m being of the order of 5 or 6.

Hence the complete virial for a real gas takes the form

$$\frac{3}{2}pV - \frac{1}{2}nmC^2 - \frac{1}{2}\sum rf(r) - \frac{1}{2}\sum rF(r) = 0.$$

In order to derive the equation of state from this expression, it becomes necessary to evaluate $\frac{1}{2}\sum rf(r)$ and $\frac{1}{2}\sum rF(r)$ in terms of properties of the molecules. The solution of this problem in the most general case applicable to all pressures, especially the high pressures, is quite difficult. The problem is very much simplified for the case of gases at ordinary pressures as Reinganum[17] has shown. He considers pressures so low that on the average but two molecules at a time come within the regions of attraction of each other. Thus the form of the theorem deduced above for pairs of molecules is strictly applicable. If the volume V of the gas were of the order $2b$ or less, the condition mentioned above would no longer be true, but for ordinary pressures, such as atmospheric, it is readily applicable. In this deduction the general form of the derivation of Reinganum's equation, as given by G. Jaeger and also K. Jellinek, will be used.

In proceeding one may follow Reinganum in assuming that:

1. The time of the impacts may be neglected, *i.e.*, one is dealing with the instantaneous forces of elastic impacts.

2. The forces of attraction decrease continuously yet rapidly with the distance and are *independent of the molecular velocities.*

Both of these assumptions are compatible with Van der Waals' theory.

3. It is further assumed that, unlike other approaches, the molecular forces in the interior of the gas are *not* mutually compensated. That is, during and between impacts the forces between two molecules are appreciable. This means that one must take account of the mutual planetary influences of the molecules on each other in the equation of state.

In this matter one deviates distinctly from the original theory of Van der Waals. In doing so, one is, however, taking account of a feature of the attractive forces which is known to exist and which turns out to be of significant magnitude. Thus the equation to be deduced should in this respect be more accurate than Van der Waals' original equation, as will be seen to be the case. It was, in fact, the neglect of this factor which made the corresponding deduction in the first edition of the Kinetic

Theory faulty and gave a value of Van der Waals' a which was constant instead of being a function of T, as is actually the case. The effect of this assumption is virtually the same effect which was observed by realizing that the number of molecules per unit area in a slab of the gas in the rigorous deduction of the pressure p', Sec. 48, was not $\frac{n}{v}df$ but more correctly $\frac{n}{v}dfe^{-u_r/kT}$.

In the deduction it will be necessary to assume for the purposes of integration that the repulsive forces become indefinitely great at distances $r = \sigma - \delta$, where δ is very small compared with σ. Again in accord with what has gone before, one must assume a gas at such a pressure that no more than two molecules interact together at any time. This means that the density of the gas must be such that the chance of three or more molecules finding themselves at such distances that the attractive forces are active is vanishingly small. It is now essential to gain a clearer concept of what is meant by a pair of molecules. Assume that about each of the n molecules, in the volume V considered, two spheres of radii r and $r + dr$ be drawn. The volume between these two spheres is then $4\pi r^2 dr$ which gives a total volume for the n molecules of $4\pi r^2 n dr$. If the volume of the gas is V, the chance that an arbitrarily chosen point lies in this volume is $\frac{4\pi n r^2 dr}{V}$. The number of the centers of the n molecules that happen to lie in these regions in the gas is $\frac{4\pi n^2 r^2 dr}{V}$. A pair of molecules is then defined as any two molecules which belong to this number which lie within the spheres of some other molecule. Since the chance of more than two molecules lying in this relation to each other is assumed vanishingly small, the number of *pairs* of molecules lying between r and $r + dr$ of each other is

$$dn = \frac{2\pi n^2 r^2 dr}{V}.$$

At this point, one must bring in the third assumption of Reinganum, *i.e.*, the assumption that the molecules of a pair are always exerting forces on each other. As in Sec. 48, one must then take account of the fact that the potential energy of a molecule in the force field of the other influences the concentration. Thus dn must be corrected by the factor $e^{-u_r/kT}$ as was the case in Sec. 48, where u_r is the *potential energy* of a

molecule in the force field of another molecule r cm away, k is the Boltzmann constant, and T is the absolute temperature. Hence one can write

$$dn = \frac{2\pi n^2 r^2}{V} e^{-\frac{u_r}{kT}} dr.$$

To obtain the repulsive virial for the gas, the quantity $rf(r)$ must be multiplied by dn and integrated over all the regions for which the repulsive forces are active. That is to say, one must integrate the quantity $dnrf(r)$ from $\sigma - \delta$ at which the repulsive force becomes infinite to σ at which this force ceases to act.

Thus one writes that

$$\sum rf(r) = \frac{2\pi n^2}{V} \int_{\sigma-\delta}^{\sigma} r^3 f(r) e^{-\frac{u_r}{kT}} dr.$$

Now, by definition,

$$u_r = \int_{\sigma}^{\infty} F(r)dr + \int_{r}^{\sigma} f(r)dr,$$

so that one can set

$$e^{-\frac{u_r}{kT}} = e^{-\frac{1}{kT}\int_{\sigma}^{\infty} F(r)dr} \times e^{-\frac{1}{kT}\int_{r}^{\sigma} f(r)\,dr}$$
$$= e^{\frac{\beta}{T}} \times e^{-\frac{1}{kT}\int_{r}^{\sigma} f(r)dr}$$

since the definite integral $\int_{\sigma}^{\infty} F(r)dr$ is a constant. Again, since σ and $\sigma - \delta$ are so close together, the r under the integral sign where it does not occur in a functional expression may be set equal to σ, a constant. One thus obtains

$$\sum rf(r) = \frac{2\pi\sigma^3 n^2}{V} e^{\frac{\beta}{T}} \int_{\sigma-\delta}^{\sigma} f(r) e^{-\left(\frac{1}{kT}\right)\int_{r}^{\sigma} f(r)dr} dr.$$

Boltzmann evaluates this integral as follows:

Set $\int_{r}^{\sigma} f(r)dr = y$, which permits one to write the integral as $\int_0^{\infty} e^{-y/kT} dy$, since at $r = \sigma$, $y = 0$, and, at $r = \sigma - \delta$, $y = \infty$.

The expression $\int_0^{\infty} e^{-y/kT} dy = kT$.

Whence one has for $\Sigma rf(r)$ the value:

$$\sum rf(r) = \frac{2\pi\sigma^3 n^2 kT}{V} e^{\frac{\beta}{T}}$$

$$= \frac{3RTbe^{\frac{\beta}{T}}}{V},$$

if one set $b = \frac{2}{3}\pi n\sigma^3$ and $nK = R$.

The virial of the attractive forces can be set as

$$\sum rF(r) = \frac{2\pi n^2}{V}\int_\sigma^\infty r^3F(r)e^{-\frac{u_r}{kT}}dr,$$

following the procedure for the repulsive virial with the appropriate changes. In this case one finds that $u_r = \int_r^\infty F(r)dr$, since beyond σ only attractive forces act. Hence

$$\sum rF(r) = \frac{2\pi n^2}{V}\int_\sigma^\infty r^3F(r)e^{-\frac{1}{kT}\int_r^\infty F(r)\,dr}dr.$$

If $F(r)dr$ is known in a specific case, the integration can be carried out. As, $F(r)$ in the general equation of state, is not specified or known, one can not proceed further with its evaluation in detail. It is, however, clear that in general the integral will be a constant containing σ, but, in view of the $1/kT$ in the exponential term, it is clear that the integral will be an expression containing T in some form. For the purposes of obtaining the equation of state in a more general form, this evaluation suffices and one can write

$$\int_\sigma^\infty r^3F(r)e^{-\frac{1}{kT}\int_r^\infty F(r)\,dr}dr = \phi(T).$$

Thus $\sum rF(r) = \frac{2\pi n^2}{V}\phi(T)$. Placing this and the expression for the repulsive virial into the appropriate places in the virial equation for a real gas written above, one has the equation of state for a real gas as

$$\frac{3}{2}pV - \frac{1}{2}nmC^2 - \frac{3RTbe^{\frac{\beta}{T}}}{2V} - \frac{2\pi n^2}{2V}\phi(T) = 0.$$

Rearranging and calling $\frac{1}{3}nmC^2 = RT$, one obtains

$$pV = RT\left(1 + \frac{be^{\frac{\beta}{T}}}{V}\right) + \frac{2\pi n^2}{3V}\phi(T).$$

$$p = \frac{RT}{V}\left(1 + \frac{be^{\frac{\beta}{T}}}{V}\right) + \frac{2\pi n^2}{3V^2}\phi(T).$$

Thus

$$\left(p - \frac{2\pi n^2}{3V^2}\phi(T)\right)\left(\frac{V}{1 + \frac{be^{\frac{\beta}{T}}}{V}}\right) = RT,$$

which to a first approximation gives

$$\left\{p - \frac{2\pi n^2}{3V^2}\phi(T)\right\}\left\{V - be^{\frac{\beta}{T}}\right\} = RT.$$

If one sets $a = \frac{-2\pi n^2}{3}\phi(T)$, and $\beta = 0$, one arrives at the usual form of the Van der Waals' equation,

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT,$$

where b was defined as $\frac{2}{3}\pi\sigma^3 n = 4\omega$.

The Reinganum equation is, however, more accurate, and it is of interest to note that it makes a a function of T and the term called b in the Van der Waals form also a function of T. It must again be emphasized that this equation is not applicable to high pressures where b is comparable with V. It is, however, an equation deduced on strictly proper assumptions, and, while in itself not perfect, it gives an equation of state based on theory which is more accurate than Van der Waals' theory but to which Van der Waals' theory is a first approximation.

51. Determination of a and b from Measurements on the Expansion Coefficients of a Gas. Evaluation of the Absolute 0 of Temperature.—Since the deviations of the true gases from the behavior of an ideal gas are caused, to a first approximation, by the constants introduced into the more correct Van der Waals equation, a study of these deviations should make it possible to evaluate these constants. Experimentally, the deviations appear in the behavior of gases with change in temperature. If the volume and pressure changes with temperature are evaluated experimentally, comparison with the coefficients for the ideal gas will permit the values of a and b to be determined from the relations to be deduced. Incidentally, it will be found essential to evaluate α, the coefficient of expansion for an ideal gas.

The value of this quantity α leads at once to the establishment of the experimental value for the absolute zero of temperature in terms of the centigrade scale.

In proceeding to the deduction, it is well to recall the definition of the coefficient of expansion for an ideal gas. As was shown in Sec. 1, the equation for an ideal gas $pv = RT$ follows at once from the experimental relation giving the volume or pressure change of an ideal gas with temperature which reads

$$v = v_0(1 + \alpha t)$$

or

$$p = p_0(1 + \alpha t).$$

Since the ideal gas has forceless molecules and the molecules have no volume, α is the same in both cases and both p and v vanish when $t = -\frac{1}{\alpha}$.

In the present case (*i.e.*, that of a real gas), however, the gas does not have the properties of the ideal gas, and its equation of state is expressed by

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.*$$

Now as RT was derived from the value of α for an ideal gas, RT is $\alpha p_0 v_0\left(\frac{1}{\alpha} + t\right)$, where α is the expansion coefficient for the ideal gas. Since $p_0 v_0$ on the kinetic theory is $\frac{1}{3}nmC_0^2$, the RT may be replaced by the expression $\frac{1}{3}nmC_0^2(1 + \alpha t)$. For the sake of simplicity in this deduction the value of C at 0°, which is denoted as C_0, will be written merely C. Hence the equation of state (for a real gas) for the present purpose takes the form given by the equation.

$$\left(p + \frac{a}{v^2}\right)(v - b) = \frac{1}{3}nmC^2(1 + \alpha t).$$

Now for a real gas the volume and pressure at 0° abs. will not be 0, for the molecular volumes and intermolecular forces exist at 0° abs. Thus the coefficient α will no longer typify the *volume or pressure coefficient* of expansion of a real gas.

* For convenience from now on the volume of the gas V will be represented by v.

The *pressure coefficient* of expansion is defined as $\beta = \frac{p_t - p_0}{tp_0}$, that is, the pressure at $t°$ less the pressure at 0° divided by t times the pressure at 0°. It is the rate of change of pressure with temperature divided by the initial pressure. To obtain this for a real gas, p_t and p_0 must be introduced from Van der Waals' equation:

$$\left(p_t + \frac{a}{v^2}\right)(v - b) = \frac{1}{3}nmC^2(1 + \alpha t).$$

$$\left(p_0 + \frac{a}{v^2}\right)(v - b) = \frac{1}{3}nmC^2(1 + 0 \times \alpha).$$

Subtracting to get $p_t - p_0$, one obtains

$$(p_t - p_0)(v - b) = t\alpha\left(\frac{1}{3}nmC^2\right).$$

Hence $\beta = \frac{p_t - p_0}{tp_0}$ is given by $\beta = \frac{\alpha}{p_0}\frac{1}{3}\frac{nmC^2}{v - b}$, but $\left(p_0 + \frac{a}{v^2}\right) = \frac{1}{3}\frac{nmC^2}{v - b}$ and therefore

$$\beta = \frac{\alpha}{p_0}\left(p_0 + \frac{a}{v^2}\right) \quad \text{or} \quad \beta = \alpha\left(1 + \frac{a}{v^2p_0}\right).$$

If α were known, then, since β is measured experimentally, knowing v and p_0, a could be determined for the gas.

Hence this equation can be of some use if α is known. To get further information, the *volume* coefficient of expansion must be evaluated in terms of Van der Waals' equation.

The *volume coefficient* of expansion for a gas is defined as

$$\alpha_v = \frac{v_t - v_0}{tv_0}.$$

Thus in analogy to the case for the pressure coefficient,

$$\left(p + \frac{a}{v_0^2}\right)(v_0 - b) = \frac{1}{3}nmC^2(1 + \alpha \times 0)$$

$$\left(p + \frac{a}{v_t^2}\right)(v_t - b) = \frac{1}{3}nmC^2(1 + \alpha t)$$

$$p(v_t - v_0, + a\left(\frac{1}{v_t} - \frac{1}{v_0}\right) - ab\left(\frac{1}{v_t^2} - \frac{1}{v_0^2}\right) = \left(p + \frac{a}{v_0^2}\right)(v_0 - b)\alpha t$$

and $v_t - v_0 = \alpha_v v_0 t$,

therefore

$$(v_t - v_0)\left(p - a\frac{1}{v_t v_0}\right) + \frac{v_t^2 - v_0^2}{v_0^2 v_t^2}ab = \left(p + \frac{a}{v_0^2}\right)(v_0 - b)\alpha t$$

$$p\alpha_v v_0 t - \frac{a\alpha_v t}{v_t} + \frac{\alpha_v abtv_0(v_t + v_0)}{v_0^2 v_t^2} = \left(p + \frac{a}{v_0^2}\right)(v_0 - b)\alpha t;$$

dividing by $v_0 t$,

$$\alpha_v\left[p - \left(\frac{a}{v_t v_0}\right)\left(1 - \frac{b(v_0 + v_t)}{v_0 v_t}\right)\right] = \left(p + \frac{a}{v_0^2}\right)\left(1 - \frac{b}{v_0}\right)\alpha$$

and therefore

$$\alpha_v = \alpha\frac{\left(p + \frac{a}{v_0^2}\right)\left(1 - \frac{b}{v_0}\right)}{p - \left(\frac{a}{v_t v_0}\right)\left(1 - b\frac{v_t + v_0}{v_0 v_t}\right)}$$

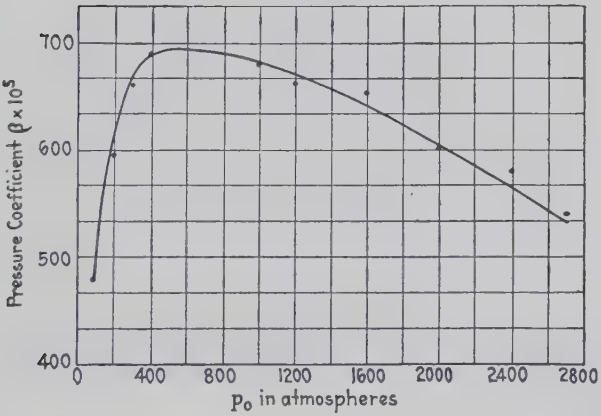

FIG. 33.

Thus α_v is a much more complicated function of α, a, and b than was β. It is seen, however, that if the constant α for an ideal gas can be evaluated for certain gases, and if, from the expression for β, a can be found for gases other than those used in getting α, then b can be found from α_v.

These two expressions for α_v and β in terms of a, b, and α merit some discussion.

First the expression leads to one result which has been verified experimentally and is hence interesting.

$$\beta = \alpha\left(1 + \frac{a}{v^2 p_0}\right).$$

Thus β plotted as a function of p_0 should vary in the following fashion: α is a constant, a is also a constant, while $p_0 v$ is nearly constant for some pressures. Hence over the range where $p_0 v$ is constant, and since as p_0 increases, the remaining v in $p_0 v^2$ decreases therefore β should start from a given value and increase. At the point where the volume becomes so small that, owing to the size of the molecules, v does not decrease as fast as p_0 increases, *i.e.*, where $p_0 v^2$ starts to increase, then β should begin to decrease. Thus a curve for β as a function of p_0 of the form shown in Fig. 33 should be obtained. The curve shown is actually one found experimentally for oxygen gas.

Again writing the expressions for α_v and β, the following cases may be discussed:

$$\beta = \alpha\left(1 + \frac{a}{v^2 p_0}\right).$$

$$\alpha_v = \alpha \frac{\left(p + \frac{a}{v_0^2}\right)\left(1 - \frac{b}{v_0}\right)}{p - \left(\frac{a}{v_t v_0}\right)\left(1 - b\frac{v_t + v_0}{v_t v_0}\right)}.$$

Case I.—If $a = 0 = b$.

The gas is ideal; $\beta = \alpha$ and $\alpha_v = \alpha$.

Case II.—If $a = 0$, $b > 0$.

Then $\beta = \alpha$ and $\alpha_v = \alpha\left(1 - \frac{b}{v_0}\right)$.

Thus α is greater than α_v. If α is obtained from β, and if α_v is measured, b may be evaluated. This case is nearly fulfilled by the gases He and H_2.

Case III.—If $a > 0$, $b = 0$.

Then
$$\beta = \alpha\left(1 + \frac{a}{v_0^2 p_0}\right),$$

$$\alpha_v = \alpha \frac{\left(p + \frac{a}{v_0^2}\right)}{p - \frac{a}{v_t v_0}}.$$

or
$$\alpha_v = \alpha\left(1 + \frac{a}{v_0^2 p} + \frac{a}{p v_t v_0}\right).$$

Whence $\alpha_v > \beta > \alpha$. Such a case might be covered by a condensible gas.

Case IV.—If, as is really the case for H_2 and He, $b > a > 0$,

then $$\beta = \alpha\left(1 + \frac{a}{v_0{}^2 p_0}\right)$$

and $$\alpha_v = \alpha\left[\left(1 - \frac{b}{v_0}\right) + \left(1 - \frac{b}{v_0}\right)\frac{a}{v_0{}^2 p} + \ . \ . \ .\ \right],$$

whence $\beta > \alpha$ and $\alpha > \alpha_v$ for $1 - \frac{b}{v_0} < 1$.

Therefore for the gases He and H_2

$$\beta > \alpha > \alpha_v.$$

The inequality in Case IV serves as a means of evaluating α practically. For H_2, α_v and β have been measured. Thus for H_2 the accurate older values for these constants found are $\beta = 0.003662$ and $\alpha_v = 0.003660$. α was taken, with a fair degree of certainty, to be 0.003661. This value of α gives a value for the absolute zero on the centigrade scale of -273.15°C. The present value is given as -273.18 ± 0.03°C. from other data.

Thus having α, a and b can be obtained. As a matter of fact, it is possible to get a and b much more accurately from other data, for the differences in α_v and β are small, and these small differences are very important in evaluating a and b. As a and b can be determined very much more accurately by methods to be discussed later, these more accurate values are at the present time inserted into the equations above and thus serve to evaluate α. Thus an accurate value of α is obtained and hence the value of T may be accurately determined. T is, however, also more accurately determined today by the Joule-Thomson effect on thermodynamic reasoning.

It also happens that both α_v and β vary with temperature in some gases. Since these equations show how α_v and β depend on a and b, the variation of a and b with temperature may be investigated. Actually, these quantities were assumed to be constants independent of p, v, and T in deducing Van der Waals' equation. A study of the variation of α_v and β with temperature indicates that neither a nor b is constant with temperature for all gases. These deviations and their significance can be much more profitably discussed in connection with other work, and it will be seen that the variations of a and b with conditions lead to a still more profound understanding of the nature of molecular collisions and structure.

52A. The Graphical Representation of the Equation of State and the Evaluation of a and b from Critical Data.—In the preceding section Van der Waals' equation was used to determine the absolute zero of temperature. In using it no attempt was made to plot it or to determine the form of the equation. Since it represents the behavior of the gases, it is best to analyze it graphically. It is seen at once that the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

is an equation in three independent variables, p, v, and T, having two constants whose relative and absolute values vary from gas to gas. To plot it for a given set of values of a and b would not give the general view of it required, particularly if a and b are not known. With the use of the calculus, a very good general idea of its shape and its significance can be obtained.

To simplify the discussion, T could be considered a constant and the attention concentrated on the relation between p and v. Then to gain a more perfect picture, this could be done for a whole series of different values of T. The curves plotted with p as ordinates and v as abscissæ, holding T a constant, are called *isothermal curves*, or *isotherms*, the term coming from the Greek *iso*, meaning equal, and *therme* (heat) temperature. They are curves of equal temperature. It is seen at once that the Van der Waals equation regarded in this way and multiplied out has the form

$$v^3p - v^2(RT + pb) + av - ab = 0.$$

It is thus a cubic equation in v. Such an equation is known from elementary algebra to have either three real roots or only one real and two imaginary roots, depending on the values of the constants—that is to say, for one value of p there will be either three real values of v or only one real value. The conditions determining these will be found later.

The Van der Waals equation may be written in the form

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

It is seen from this that for values of v near b the pressure p approaches infinity. For values of v smaller than b the equation has no physical meaning, as p is then negative. Furthermore, if v becomes very large, p becomes vanishingly small. Thus the

two extremes of the curves are definitely determined, for, as v approaches b, p becomes infinite, and as v approaches infinity, p approaches zero asymptotically. In the extremes the curve descends in p as v increases, approaching zero in the limit. It is therefore part of the way concave upward. In between, it may have maxima and minima, and, in fact, the three roots lead one to expect, under some conditions, a complex course.

The maxima and the minima are found by setting the first derivative equal to zero, and solving the equation; that is, in finding the points where dp/dv is zero.

$$\frac{dp}{dv} = \frac{-RT}{(v - b)^2} + \frac{2a}{v^3}.$$

In the expression above, dp/dv is negative for values of v that are very small, for near b the term $RT/(v - b)^2$ can become greater than the $2a/v^2$ term. Again, dp/dv is negative for very large values of v, for in this case, since v^3 increases more rapidly than v^2, the second term becomes less than the first. Thus for large and small values of v the first derivative is negative, meaning that the curve slopes toward increasing v. Between large and small values of v the dp/dv term is positive under some conditions and hence the curve slopes to the decreasing v's.

The values of v for maxima and minima are given by solving the equation above when $dp/dv = 0$. This solution yields an equation in a, b, v, and T of the form

$$T = \frac{2a(v - b)^2}{Rv^3}.$$

This is a cubic in v and thus has three real roots or one real and two imaginary roots. That is, there are either three values of v which satisfy this equation for maxima or minima, or there is only one. Thus two conditions exist for the curves, that is, they have either three points where $dp/dv = 0$ or only one. Now the course of the equation which was deduced from the value of the sign of dp/dv for values between $v = b$ and $v = \infty$ indicates that the curve descends with increasing v to a minimum, rises when dp/dv is positive to a maximum, and finally descends asymptotically to 0 at $v = \infty$. There appear to be between $v = b$ and $v = \infty$ then only one maximum and one minimum. The three roots of the equation for maxima and minima indicate, however, three points at which $dp/dv = 0$.

Thus one of the three points must lie at values of v less than b. It is therefore of no importance for the present analysis. That the third root lies in this region can be shown by transforming the equation for maxima and minima to one whose origin is not at 0 but at b. If this is done the expression becomes $RT(b + w)^3 - 2aw^2 = 0$, where $w = v - b$. This equation expanded gives

$$w^3 + \left(3b - \frac{2a}{RT}\right)w^2 + 3b^2w + b^3 = 0.$$

Now a well-known relation in the theory of equations says that for a cubic the product of the three roots must be equal to the negative value of the last term, that is, that the three roots w_1, w_2, and w_3 multiplied together should be equal to $-b^3$. But in the equation above the last term is positive and hence one of the three roots must be negative. In such an equation for the case that two of the roots are imaginary and one only is real the relation further indicates that the real root is negative. Hence referred to b as origin, one of the three points at which dp/dv is 0 must always lie at negative values, that is, one of the three maxima (or when there is only one real maximum or minimum that one) must lie at values of v smaller than b. This agrees with the conclusions arrived at from the slopes, namely, that the isotherm has either no maximum or minimum or only two. The shape of the isotherms must therefore take the form either of the curve marked 13.1° or 100.1° in Fig. 34 for the cases where there are three real roots and one real root respectively. It is seen that this curve also fulfils the condition for three real roots of Van der Waals' original equation, for a given value of p will intersect the curve in three places. To find the values for the maxima and minima, numerical values for a, b, and T would be required. By evaluating d^2p/dv^2 for these points, one would find, from the sign of d^2p/dv^2, to which value of v the maximum belonged. Letting d^2p/dv^2 equal zero would determine the position of the point of inflection between the maximum and minimum.

Now the expression for the maxima and minima,

$$T = \frac{2a(v - b)^2}{Rv^3},$$

is a continuous function of v. For values of v small enough to approach b it has a small value, and for values of v which are

very great, since v^3 increases more rapidly than $(v - b)^2$, it has small values. Between the two extremes it has a maximum value. Physically, there exist values of T above this maximum

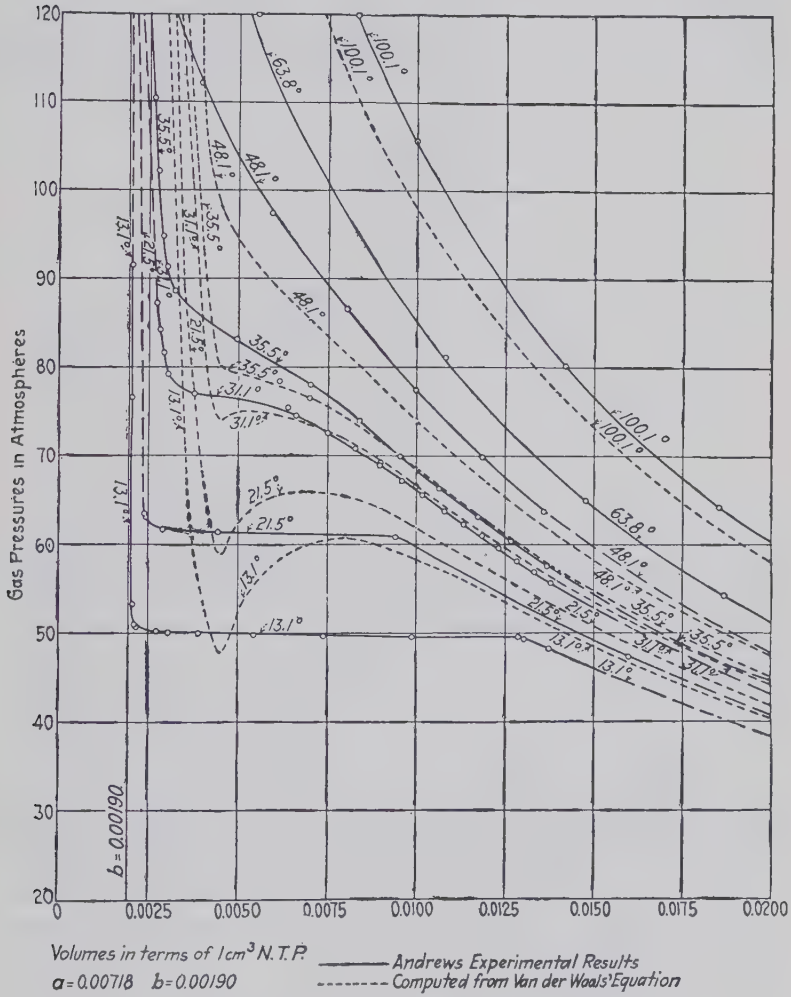

FIG. 34.

which must lie above this curve, that is, there are conditions of temperature in which the three maxima and minima do not exist. At such temperatures, however, the isotherms still exist, but they can have only the one minimum; and this one has values of v less than b. In such curves the sign of dp/dv is always negative,

T being so large that $2a/v^3$ can never exceed $RT/(v-b)^2$. The curve then slopes down continually to higher values of v. The particular temperature at which the curve ceases to have one minimum and one maximum above $v = b$ can be called the *critical* temperature. The value of T_c when the function is a maximum is found by setting dT/dv equal to zero and solving for v.

$$\frac{dT}{dv} = \frac{-2a(v^2 - 4vb + 3b^2)}{Rv^4} = 0,$$

$$v^2 - 4bv + 3b^2 = 0,$$

$$(v - 3b)(v - b) = 0,$$

$$v_c = 3b,$$

or

$$v_c = b.$$

For $v_c = b$, T is zero and this is a minimum. Thus the maximum is at $v_c = 3b$.

Accordingly, T_c can be found at once to be

$$T_c = \frac{2a(3b - b)^2}{R(3b)^3} = \frac{8ab^2}{27Rb^3} = \frac{8a}{27Rb}.$$

Hence there is a value of T depending on the ratio between a and b for which the curves pass into curves having no point of inflection.

Thus if a family of isotherms were plotted for the Van der Waals equation at different values of T, it would be found that above the value T_c the curves were simple curves dropping down to 0 at great values of v with no points of inflection as in the curve for 100.1° and 48.1° (Fig. 34). Below this value of T the curves have a minimum, a maximum, and a point of inflection. At the temperature T_c the curve passing through it has the maximum, minimum, and point of inflection lying infinitely close together. Hence this condition should make it possible to find a series of relations between p_c, v_c, and T_c and the constants a and b at this point. To find these, merely three equations need be used:

$$p = \frac{RT}{(v - b)} - \frac{a}{v^2}, \tag{1}$$

the original equation.

$$\frac{dp}{dv} = \frac{-RT}{(v - b)^2} + \frac{2a}{v^3} = 0, \tag{2}$$

the expression for the maximum and minimum which now lie at the same point.

$$\frac{d^2p}{dv^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0, \tag{3}$$

the expression for the point of inflection.

Since maximum, minimum, and point of inflection lie together, Eqs. (2) and (3) may be written in the forms

$$RT_c = \frac{2a}{v_c^3}(v_c - b)^2,$$

$$RT_c = \frac{3a}{v_c^4}(v_c - b)^3,$$

where T_c and v_c now correspond to the same isotherm, the critical one. For this isotherm Eqs. (2) and (3) can be combined, since $RT_c = RT_c$.

Therefore $$2a = \frac{3a(v_c - b)}{v_c}.$$

Therefore $v_c = 3b$.

This was found before as the condition for a maximum T_c for which three maxima or minima ceased to exist. From Eq. (2) and the value for v_c above,

$$\frac{dp}{dv} = \frac{-RT_c}{4b^2} + \frac{2a}{27b^3} = 0.$$

Therefore $T_c = \frac{8a}{27Rb}$.

Finally, from T_c and v_c one has $p_c = \frac{8a}{54b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$.

Thus one has a set of three equations between T_c, v_c, and p_c and a and b.

$$v_c = 3b,\ T_c = \frac{8a}{27Rb},\ \text{and}\ p_c = \frac{a}{27b^2}$$

and if T_c, v_c, and p_c can be measured one ought to get a and b.

Now the question arises, Do real gases follow these laws? If this is so, it should be possible to evaluate a and b either from the isotherms or from values of p_c, T_c, and v_c taken from observations.

Van der Waals, who as a mature man left business to undertake scientific study, deduced his now famous equation in his doctor's dissertation at Leyden in 1873. Attempts at bettering the

ideal gas equation had first been made by Clausius (see Sec. 18), who introduced the correction for the volume of the molecules into the equation by writing $v - b$ in place of v, and by Hirn, who in 1864 added an expression to the pressure term to take account of the attraction of the molecules. This term, however, did not give the variation of the force with the volume. It was by a consideration of Laplace's theory of surface tension that Van der Waals supplied the missing relation and completed the theory. About ten years previous to this, Andrews studied a peculiar phenomenon first observed by Cagniard de la Tour. This was that if a tube containing liquid carbon dioxide were heated gradually, a temperature was reached (31.1°) at which the meniscus dividing the liquid and gaseous phases disappeared. Investigation showed that no matter what the pressure became above this temperature the CO_2 which had been partly in the gaseous, partly in the liquid phase below this point changed to a homogeneous, transparent state in which there was no indication of the gas and liquid. The temperature at which this occurred was called the critical temperature. This curious observation directed attention to the behavior of gases in general at the higher pressures, and other gases like SO_2 were found which showed this behavior near ordinary temperatures. Today, this temperature has been determined for most of the well-known gases and vapors. Andrews began a series of measurements extending from 1863 to 1876, in which he studied the behavior of the isotherms of CO_2 at various temperatures and up to pressures of 200 atmospheres (atm.). These data gave Van der Waals the material upon which to test his theory.

Van der Waals first used the accurate measurements of Regnault on the isotherms of CO_2 which were carried to pressures of 27 atmospheres. Solving for a and b, using the methods depending on the pressure and volume coefficients, he estimated a to be 0.00874 atm. cm^6, and b to be 0.0023 cm^3. Introducing these values into his equation, he was able to obtain a closer agreement between his curve and Regnault's experimental points than Regnault obtained with his empirical equation. He then applied this equation to the computations in the region of Andrews' measurements. In this case the agreement was not so striking. In fact, the comparison of the computed curves and the observed curves of Andrews are not given in texts because of the discouraging nature of the agreement. It seems, however,

that the direct comparison is of sufficient value in indicating the strength and the deficiencies of the theory to merit reproduction.

To compute the isotherms it is best to use the values of a and b given by the critical data obtained by Andrews, since these are more accurate than the values deduced from Regnault's curves. Using these values, it is then equivalent to fitting the system of theoretical isotherms to *one point*, the *critical point*, on the observed system of isotherms. Andrews obtained for CO_2 the following values: $T_c = 31.1°C.$, $p_c = 73$ atm., and $v_c = 0.0066$ cm^3 for a cm^3 of gas at N.T.P. Before using these one might compare these values with those computed by Van der Waals from the equation using the a and b taken from Regnault's data, namely, $a = 0.00874$ and $b = 0.0023$.

$v_c = 3b$, $v_c = 3(0.0023) = 0.0069$ cm^3 *computed,* 0.0066 cm^3 *observed.*

$$T_c = \frac{8a}{27bR} \qquad R = \frac{1^*}{273} \qquad T_c = \frac{8(0.00874)}{27(0.0023)\frac{1}{273}} = 307°\text{abs.}$$

$T_c = 34°C.$ *computed;* $31.1°C.$ *observed.*

$$p_c = \frac{a}{27b^2} = \frac{0.00874}{27(0.0023)^2} = 61 \text{ atm. computed; } 73 \text{ atm. observed.}$$

For the computations of a and b from Andrews' results it is best to use the equations, $T_c = \frac{8a}{27bR}$ and $p_c = \frac{a}{27b^2}$, since v_c was difficult to obtain with certainty from the measurements, while p_c and T_c could be accurately measured. These give $a = \frac{27R^2T_c^2}{64(p_c)}$ $= 0.00717$ atm. $\times$ cm^6 and $b = \frac{RT_c}{8p_c} = 0.00191$ cm^3. As a partial check on these values, b can be compared with the observed $v_c = 0.0066$. Since $v_c = 3b$, the data give 0.00573. Thus there is some discrepancy between the values which may be attributed to errors in measuring v_c as well as errors in the theory of the equation to be discussed later.

With the aid of these constants, the isotherms may be computed from Van der Waals' theory as follows, taking 0.00718 for a and 0.00190 for b:

$$\left(p + \frac{0.00718}{v^2}\right)(v - 0.0019) = RT.$$

* This follows since $pv = RT$ if p is 1 atm. and $v = 1$ cm^3, $R = \frac{1}{T} = \frac{1}{273}$.

Now if the gas were ideal (*i.e.*, a and b were 0) and p were expressed in atmospheres while v was taken as 1 cm^3, pv would be unity. Thus RT would be unity. At 0°C. and 760 mm pressure R would be $\frac{1}{273}$ for this gas. Thus for the ideal gas $pv = \frac{T}{273}$. For the real gas with a and b finite, however, at 0°C. and 1 atm. the true p and the true v are given by the above. Hence, the above equation for 1 atm. and 1 cm^3 becomes

$$(1 + 0.00718)(1 - 0.0019) = 1.0053.$$

Therefore, in order to compute p and v the equation becomes

$$\left(p + \frac{0.00718}{v^2}\right)(v - 0.0019) = 1.0053\frac{T}{273}.$$

Hence, by putting in the values of T, the absolute temperature, and introducing values of v, the equation may be solved for p. Taking the values of T and v corresponding to Andrews' experimental isotherms for 13.1, 21.5, 31.1, 35.5, 48.1, and 100.1°, the Van der Waals isotherms were computed from the above equation. The resulting dashed curves may be seen in comparison with Andrews' actual curves in full lines in Fig. 34.

It is observed at once that in this region the close agreement that Van der Waals found for Regnault's results does not exist between the observed and computed values. It is, however, seen that, leaving a certain feature of the low-temperature isotherms aside (*i.e.*, the maximum and minimum), the general shape of the curves and the evolution of their form with temperature are strikingly similar. The nature of the similarities indicates that qualitatively the phenomenon is represented by the Van der Waals equation. The cause for the agreement of Regnault's values together with the apparent failure here can be easily seen by looking at the equation as used for computation.

$$p = \frac{1.0053\left(\frac{T}{273}\right)}{(v - 0.0019)} - \frac{0.00718}{v^2}.$$

It is seen that p is given by the *difference* of two terms. These terms for small values of v are especially large and a small change in a or b will make an enormous change in p. Thus unless a and b were closely constant and known to several significant figures an accurate superposition of the curves in this region would be

impossible. When v, however, is larger, say near 1 or 2 atm., the corrections a and b become insignificant. Errors in their values are negligible and a close agreement is to be expected. Van der Waals, who was interested in establishing his theory, did not publish curves of this sort. Instead, he assumed the value of a taken from Regnault's values. Then, taking p and v from Andrews' results, he computed the value of b. The values found for b varied between 0.0025 and 0.0015 in extreme cases, while they lay close to the value 0.0023 from Regnault's work, when data taken for v greater than 0.004 cm^3 were used. Now it can be seen from Secs. 19 and 49 on the value of Van der Waals' b that if v is less than $2b$, the spheres of exclusion of all the molecules must interpenetrate. Thus, on a collision, the average distance of approach of molecules is decreased and the shortening of the free path is changed. This change is of such a nature that b is no longer 4ω, but less. Hence, the rapid decrease of b with values of v below 0.004 cm^3 is a direct consequence of the kinetic theory and was to be expected. Thus Van der Waals' initial assumption that b was constant independent of v was not quite correct in the extreme case of Andrews' measurements. Neglecting this deviation, it can be seen that the values of b computed by Van der Waals from Andrews' results show a fair constancy, and the sensitiveness of the plotted curves to these small deviations is demonstrated.

Before going on to discuss more in detail the causes for deviation, the apparently most glaring discrepancy must be discussed. The experimental curves of Andrews below the critical temperature do not show the maxima and minima exhibited by Van der Waals' equation. Below the critical temperature the flat portions of Andrews' curves mark the point at which visible condensation was taking place. In the theoretical equation this discontinuity does not occur. In looking at the physical significance of the region lying between the maximum and the minimum of the theoretical curve, it is seen that it represents a region where with decreasing volume the pressure is falling. Thus the maximum is a region of unstable equilibrium, for as soon as it is reached the volume decreases of its own accord, since the pressure is not needed to maintain the small volume. It is not surprising that this region cannot be studied experimentally. Neither can the other regions near the maximum and the minimum be studied because of the instability of the gas in contact with its environ-

ment. In this case, however, it is the adhesive forces of the walls which act to cause condensation of the liquid on them before the maximum is reached. Actually, in certain cases where great care is used in reaching the condition the curves can be followed beyond the straight linear portions observed by Andrews, that is, in certain cases, with supersaturated vapors and supercooled gases condensation is avoided temporarily. These represent points along the isotherms reaching into the region discussed but not to the maximum or minimum. This state is, however, so unstable that sudden mechanical shocks, particles of dust, or any slight disturbances cause almost explosive condensation. It is obvious that it is impossible to carry on accurate measurements in this region. Thus the failure to find the maxima and the minima of the theory is not a weakness of the theory but lies in technical difficulties involved in making measurements where external agencies such as the walls do not intervene. Above the critical temperature, of course, this difference disappears. No liquid can exist there and the theoretical and observed isotherms could be made to agree with remarkable precision by properly evaluating a and b for these conditions.

Aside from the deviations of the Van der Waals equation due to conditions not envisaged by the theory and to experimental difficulties (effect of volumes less than $v = 2b$ and condensation on the walls), certain other difficulties make themselves known through the inconsistencies of the order of tens of per cent in the values of a and b, as derived from different sources (*i.e.*, isotherms and the quantities p_c, v_c, and T_c), and the failure of the data fitting a curve at one temperature to apply at another temperature. These are the real deviations of Van der Waals' equation from the true behavior of gases. Such deviations lie in a true variation of both a and b with temperature and perhaps volume. As was seen in the derivation of a from the theory of surface tension, and of a and b from the theorem of the virial, both a and b are temperature dependent. This effect in a is due to the action of the attractive forces over finite distances in changing the concentrations of the molecules. The higher the temperatures the less effective these concentration changes, and thus a is a function, $\phi(T)$, decreasing as T increases. The changes of b logically arise from the assumption that the diameter of the molecules in impact is not just σ. It comes from the fact that the repulsive forces become indefinitely great only

at $\sigma - \delta$ where δ is a small quantity, while they extend to σ (see Sec. 50). That an effect such as is found from this assumption must occur for real molecules follows from the fact that the repulsive forces on approach, while varying rapidly with decreasing distance between molecular centers, do not vary infinitely rapidly. Hence the closeness of approach is a function of the energy of impact, and σ and thus b is slowly but definitely temperature dependent. Thus it is to be expected that values of a and b for one isotherm will not fit those for another isotherm at a different temperature. Furthermore, since both $f(r)$ and $F(r)$ are different for different individual gases, the nature of the variation will not be the same for different gases. Hence it is here that one must depart from a single equation of state for real gases applicable in *general* form to any gas and use individual equations differing in detail and applicable only to single gases.

Again it is quite probable that variations of a and b may not be caused by temperature alone. It was seen that b certainly varies with volume when v approaches $2b$, and that Reinganum's equation was deduced for gases where there were only two molecules interacting at any one time. Hence certainly b and possibly a may be volume dependent over large ranges of volume or pressure. Thus one can explain the major features of the departure of the Van der Waals equation curve from the real curves for gases. While it is perhaps futile to discuss these deviations more in detail, an idea of their nature can be gained by regarding a table prepared by Jellinek[9] in his "Physical Chemistry," vol. 1, Part I, page 391. A similar table prepared more recently by Jabloczinski (*Phys. Z.*, **33**, 536, 1932) covers the same ground. In Jellinek's table, given below, are shown the values for a computed to cause a fit of the observed and calculated isotherms for a fixed value of b at different pressures, using Andrews' data for CO_2. Next them are shown the values of b required to cause a fit at a constant value of a for the same temperatures.

Temperatures, degrees C.	$b = 0.0023$, curves fit for a	$a = 0.008497$, curves fit for b
6.5	0.008497	0.0023
64.0	0.007529	
100.0	0.006798	0.0032

Thus the equation fits for either b constant and a varied, or a constant and b varied. From 6.5 to 100° the a values vary 20 per cent when b is constant, and for a constant the b values may vary by 30 to 40 per cent in this same range. It is seen that for constant b, a *decreases* as T increases as was inferred above, while for constant a, b *increases* as T increases. Doubtless both a and b vary with T and it is futile to speculate further as to the relative importance of variations of a and b, though at lower pressures in CO_2 a might be assumed to vary more rapidly than b.

It is thus seen that considerable caution must be used in comparing values of a and b, and the molecular constants derived therefrom when they come from different methods of measurement. First, one must be assured that the conditions of p, v, and T are comparable. Then, one must be sure that the methods are capable of attaching exactly the same meaning to the constants involved as yielded by different measuring procedures. Thus it is to be expected that given the same conditions of p, v, and T, the values of a and b from the isotherms and from the Joule-Thomson experiment might agree, while it is impossible that the values of a and b from critical data should agree with values inferred from the first two procedures. Again, it is possible to deduce the value of σ from transfer data such as viscosity. Care must be taken to make sure that the quantity called σ in viscosity measurements is the same quantity σ as inferred from the values of a and b derived from the equation of state.

Probably the safest procedure in the use of molecular data is to forego recourse to the approximate values of a and b and thus also the approximate values of molecular diameters, etc., and to utilize the laws of force of the particular molecular species. Studies of the temperature variation of the coefficients of Van der Waals' equation in its extended form by Kammerlingh-Onnes and Holborn and Otto have led to an evaluation of the laws of repulsive and attractive forces [$f(r)$ and $F(r)$] for individual species of atoms and molecules. A similar evaluation for the repulsive forces $f(r)$ from the coefficient of viscosity resulted from the remarkable studies of Sutherland, Chapman, and Enskog. The laws of force obtained are in application distinctly more accurate than are the approximate constants discussed, and their use gives a better insight into the real mechanisms occurring. At times,

however, they lead to unnecessary mathematical complications where only approximate results are required. It is therefore appropriate that a brief discussion of the nature of atomic force fields be given at this point.

52B. Nature of Atomic Force Fields.—Atoms are structures consisting of a massive nucleus responsible for 99.9 per cent of the inertia of the atoms, having minute dimensions ($< 10^{-12}$ cm) and carrying Ze units of positive charge, where Z is the number of the atom in the periodic table and e is the unit electrical charge, 4.77×10^{-10} electrostatic unit (e.s.u.) (see also Chap. IX, Sec. 91, and Chap. X, Sec. 101). In molecules, which are combinations of atoms, the nuclei of the constituent atoms occur separated by distances comparable in order of magnitude with the molecular *radii*. In neutral atoms or molecules the nuclear positive charges are surrounded by Z negative electrons. In atoms these Z electrons are distributed in various regions about the nucleus which can be called shells (K, L, M shells giving the K, L, M X-rays) whose boundaries are rather indefinite but whose average locations are found at rather widely different distances from the nucleus when several shells are present. Thus in argon, $Z = 18$, the nucleus is surrounded by an inner shell of two electrons about 2.5×10^{-10} cm from the nucleus, a shell of eight electrons in two subgroups about 1.2×10^{-9} cm distant, and another shell of eight electrons distributed like the first eight at about 1×10^{-8} cm from the nucleus.

In each of these shells the electrons in turn appear in regions of indefinite outline but whose average position would closely resemble an orbit of elliptical or circular type, different orbits being oriented in various specified directions in space. In some atomic configurations such as the inert gases, these electron shells and individual paths are quite symmetrical. In other atoms this is not true. When atoms unite to form molecules, the nucleii are generally separated by distances of the order of 5×10^{-9} cm so that the inner shells of electrons belong to the individual atoms. However, the outermost shells, in part at least, are held by the atoms in common. Hence in the outer shells quite a range of possible asymmetries are found, owing to the distribution of positive charges as well as of electrons. They range in asymmetry from such unsymmetrical configurations as HCl to the rather highly symmetrical N_2 molecule. Between the electrostatic charges in the atoms the law of force is

the Coulomb law, *i.e.*, the individual charges e attract or repel each other according to the law $f = \pm e^2/r^2$. In addition, owing to electronic motions, there are magnetic moments in the atoms which in many cases are not canceled out (see Secs. 100 and 101). The magnetic forces are, however, subordinate in importance to the electrical by an order of magnitude or more in most cases. Were atoms perfectly symmetrical arrangements of electrical charges about the nuclei, *i.e.*, so that the electrical shells were uniform spheres surrounding the positive nuclei as centers, there would *ideally* be no electrical forces between atoms at a distance. As in fact this is never exactly true, there are electrical asymmetries. These lead in some cases to what is the equivalent of a positive and a negative charge e, separated by a finite but small distance l. Such an arrangement may be considered as an electrical dipole or doublet which, in close analogy to the magnetic dipole or magnet, has a *moment* $\mu = el$. Thus for instance, in HCl there is a dipole of moment $\mu = 1.03 \times 10^{-18}$ e.s.u. $\times$ cm equivalent to a charge $+e$ and a charge $-e$ separated by 0.2×10^{-8} cm in a molecule with nuclei 1.276×10^{-8} cm apart. As is known, magnets having a moment $ml = M$ when they are coaxial with their centers r cm apart, where $r >> l$, attract or repel each other by a force $F = 2M/r^3$. In an exactly similar manner two electrical dipoles would attract or repel each other at a distance r with a force of the form $f = a\mu/r^3$, where the constant a and the sign depend on the orientation of the axes. In free atoms or molecules of a gas such forces would mainly be attractive as the repulsive forces due to antiparallel orientations would cause rotations tending to give attractive alignments of lower potential energy. In more symmetrical molecules alternate charges at the corners of a square or at the corners of a cube would give arrangements called quadripoles and octopoles. These exert attractive forces which fall off more rapidly with r, *i.e.*, of the form a_1/r^4 and a_2/r^5, respectively. All these types of forces were at one time in general held responsible for the attractive forces between molecules. Lately it has become apparent that, while dipoles, quadripoles and octopoles do perhaps exist and play a part, the attractive forces are arrived at in a slightly different fashion. Consider such a symmetrical configuration as argon. Two argon atoms despite their general symmetry are not continuously or completely symmetrical. As they near each other, a slight

asymmetry of one atom giving a weak dipole will produce a field at the other atom proportional to $1/r^3$. This field will in turn distort atom 2 so as to produce a weak dipole in it. This dipole will in turn react to increase the original dipole in atom 1 and perhaps make it more lasting if only transitory. Thus the two atoms will mutually induce dipoles in each other and thus attract even in the absence of any net permanent dissymmetry. It is seen that such forces will vary as $1/r^6$, for in this case the inducing fields vary as $1/r^3$ and the force between dipoles produced by these fields will vary as $1/r^3$ so that the resulting force will vary as $1/r^3 \times 1/r^3 = 1/r^6$. Such a law actually appears to be the attractive law of force inferred from experiment for many gases. Doubtless the inverse-fifth-power law would serve nearly as well, but the inverse-sixth-power law appears today to be more nearly theoretically correct and to have more basis in fact. In many cases an inverse-fifth-power law has been used as it leads to greater mathematical simplicity.

The repulsive forces between atoms and molecules must be ascribed to a different type of action. As two atoms approach to distances between centers of from 2σ to σ, where σ is the molecular diameter, the distances between the outer negative electronic shells decrease from about σ to 0, while in the same time the positive centers of force, of course, approach from 2σ to σ. Thus the repulsive forces of the electron shells rapidly increase toward infinite values as the centers approach to a distance σ, if there is no distortion of the shells. Actually the repulsive forces somewhat distort the outer shells, but even here limits are reached so that ultimately for any impact the potential energy of distortion equals the kinetic energy of impact and the centers start to recede. It is clear that repulsive forces of this nature which are feeble at a distance of 2σ and reach indefinitely large values at a distance slightly less than σ must vary very rapidly with r. Thus the repulsive forces have in the past been set as following a law of the form $f(r) = 1/r^n$ where n varies from 9 to 15. Such laws have been found to give relatively satisfactory values when used in equations applied to actual gases. There is, however, little if any theoretical justification for their use except that of mathematical simplicity and that they are convenient for representing very rapid increases of the repulsive force with distance at a certain distance σ of separation. The applications of the new wave

mechanics to the study of the interactions of simple atomic systems have shown on very general grounds that the law of repulsive force must be more of the form $f(r) = De^{-\lambda r}$, where the constants D and λ are not defined but can be evaluated from experimental data. At the present writing little has been done in the application of this law to the case of individual gases, but the little done appears to yield satisfactory results.

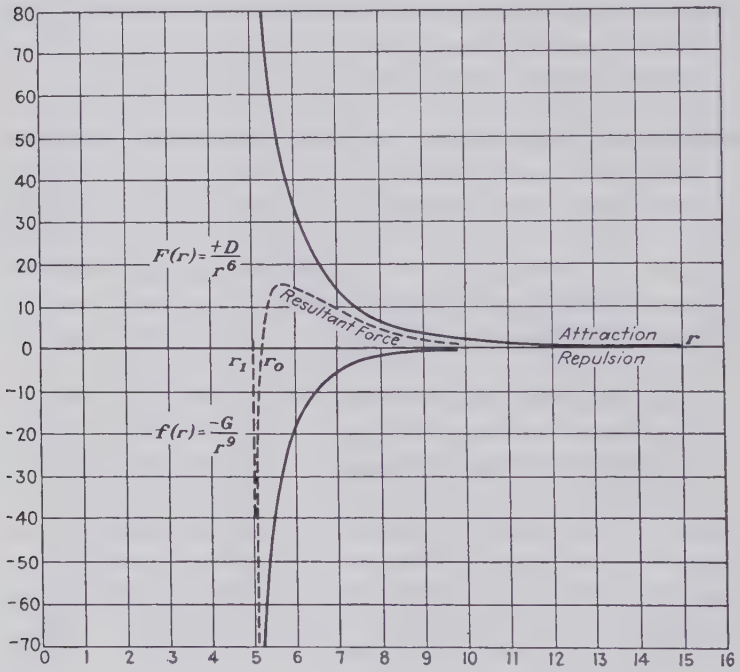

FIG. 35.

To sum up then, one can assert that in general the attractive and repulsive interatomic forces are largely of an electrical nature; that the attractive forces are of a polar or induced polar nature of the form $F(r) = +D/r^m$ where $m = 5$ or 6, and that the repulsive forces are also electrical and of a form $f(r) = -G/r^n$, where n is high and of the order of 9 to 15, or perhaps even better that they have the form $f(r) = -D_1e^{-\lambda r}$ as indicated by the wave mechanics, the inverse power law being a first-order approximation to the more correct wave-mechanical expression. To gain an idea as to how repulsive and attractive forces simultaneously acting on two molecules cause the mole-

cules to behave, one can plot the nuclear distances r as abscissæ against the positive attractive forces $F(r) = +D/r^m$ and the negative repulsive forces $f(r) = -G/r^n$, as ordinates, for example, setting $m = 6$ and $n = 9$. On plotting these laws, one sees that the resultant force $\phi(r) = D/r^6 - G/r^9$ takes the form of the dashed curve of Fig. 35 which is simply the difference of the two terms. It is seen at once that $\phi(r)$ is negative and very great for values of r but slightly less than r_0 where $\phi(r)$ cuts the axis of abscissæ. From r_0 on, to greater values of r, $\phi(r)$ increases to a maximum to decrease thereafter asymptotically to 0. The distance r_0 is the equilibrium distance of the two nuclei at $\phi(r) = 0$. It represents the "diameters" of the molecules at rest. If the molecules collide so that they exert a force due to the energy of impact, the centers will approach to a point r_1 determined from the energy at impact and the force $\phi(r)$. As the repulsive force increases very rapidly with distance, a great change in energy of impact will bring the nuclei but little closer together. Thus the distance $\overline{r_1 r_0}$ is really the δ used in the derivation of the equation of state from the theorem of the virial. It is slightly temperature dependent and quite small. Thus the molecules *appear* to have a fairly definite but not precisely fixed "diameter" of the order of r_0. Another feature of the curve for $\phi(r)$ is that it is asymmetrical about r_0. Thus for atoms or molecules bound together at r_0 any disturbance of the system by kinetic impacts will cause the two units to experience a force that is *not* proportional to the displacement, and the oscillations of any considerable amplitude will be anharmonic. Finally since the force increases less rapidly to the right of r_0 than it increases in a negative sense to the left, as oscillations become more and more violent, the swings to the right, which have an energy equal to those to the left, will carry the center farther to the right of r_0 than they do to the left. Hence the *center of oscillation will be displaced toward greater values of r than* r_0. In the rows of molecules or atoms in a solid this means that the spacing of the centers of oscillating pairs at higher temperatures will be greater than at low temperatures and the body will *expand* on heating. For a study of the solid state, and especially for molecular vibrations, it is most instructive to plot not only the force curves but also the potential-energy curves which are given by $E_r = \int +F(r)dr$ and $\epsilon_r = \int -f(r)dr$, and plot the resultant curves. This is very simply done, as in the energy curves

the powers of the exponents m and n are only reduced by unity, the signs are reversed, and the resultant energy curve has a form somewhat similar to that for $\phi(r)$ only that it is negative and inverted. In this case the minimum of the resultant potential-energy curve falls at the r_0 for the force curves.

53. The Joule-Thomson Effect Interpreted by Van der Waals' Equation.—The values of the constants a and b of Van der Waals' equation may be determined in still another fashion. This is by means of the so-called "porous-plug" experiment of Joule and Thomson. Inasmuch as the interpretation of this effect by means of Van der Waals' equation leads to a clear explanation of an otherwise complex phenomenon, it is of considerable value to give the analysis.

If a gas expands by a volume v against an outside pressure p it does work equivalent to the product pv. The energy for doing this work comes from the heat energy (*i.e.*, the kinetic energy of the gas molecules). The expanding gas then does work but loses heat energy in the process. If the process is so conducted that no heat flows in, the gas is cooled. This external work performed would be the only work performed by an ideal gas. In a real gas, however, the molecules attract each other and the expansion of the gas against the internal pressure also consumes energy. In this case the gas would also be cooled and the work it did would result in increasing the potential energy of the gas, for if the gas were left to itself so that the attracting forces alone could act it would contract and the work of contraction would again come out as increased heat energy of the molecules. Thus for real gases an expansion against external pressure would result in a cooling, due to two causes—one the external work done, the other the work done against the internal pressure. To see whether the ideal gas law held or whether there were internal forces of attraction, Gay-Lussac performed the following experiment: Two carefully heat-insulated vessels A and B of Fig. 36 were connected by a valve V. One was filled with compressed air, the other was evacuated. A thermometer was placed in each. When they had reached the room temperature, the valve was opened and the air in A flowed into B. After the first air had entered B, the succeeding air expanded from A and compressed the air in B. If the process was done so quickly that heat did not flow into or out of the system, the air in A should have cooled and the air in B should have been warmed by the work of

compression. Since the heat of compression in B came from the heat which was present in the gas in A, no loss or gain from the environment having occurred, the heating in B should equal the cooling in A if no internal work was done. If work had been done against molecular attractions, then, since before expansion the gas had the volume A while afterwards it had the volume $A + B$,

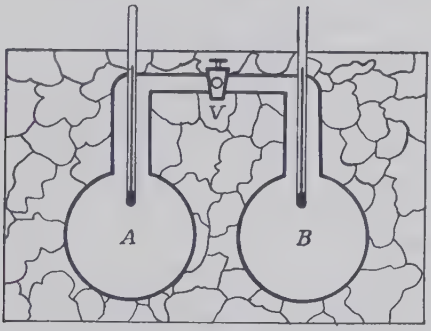

FIG. 36.

there should have been a cooling due to the internal pressure p acting against the expansion from A to $A + B$. The gain in heat in B plus the loss in heat in A should not then have equaled zero but should have been less than zero, by an amount depending on the specific heat of the gas, the volume changes, and the magnitude of the $p' = a/v^2$ pressure term of intermolecular attractions. Since a/v^2 is small, and since the thermometers

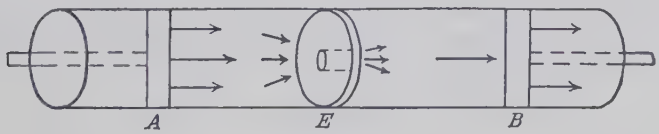

FIG. 37.

available to Gay-Lussac had a high heat capacity and were inaccurate, it was to be expected that he found the sum of the temperatures in A and B equal to zero.

A similar result was also obtained by Joule. In this experiment the vessels A and B were placed in a water bath. Thus if the heating in B were less than the total cooling due to the expansion in A and the work against the internal pressure, the net cooling should have lowered the temperature of the bath.

Again, because of the large heat capacity of the bath and the inadequacy of his thermometers, no cooling was observed.

Later Joule again attacked the problem with the help of William Thomson, Lord Kelvin. On this occasion they used a method involving the continuous expansion of the gas through a porous plug of cotton wool. In this instance they obtained a positive result and the experiment has become famous in history as the Joule-Thomson "porous-plug" experiment.

The theory of the method is as follows: Consider a cylinder with a partition E in which there is a small hole. Also imagine two pistons A and B, one on each side of the partition E in Fig. 37. If a gas be in the volume AB and the piston A be moved in slowly, the air in AE will be compressed. As a result, it will flow through E into EB. If B be connected to some mechanism so that it exerts a constant pressure on the gas E which is less than the pressure on A, the gas will flow from AE to EB and will move B outward, that is, it will do external work on B. Experimentally, this is accomplished by letting air in an external reservoir flow through a small opening continuously; the pressure difference between AE and EB causing the flow, and the pressure in EB giving the constant back pressure. If O is the area of the cylinder then p_1O is F_1, the force on A, and p_2O is F_2, the force on B. If A moves x_1 cm and B moves x_2 cm, then the work done is $F_1x_1 = p_1Ox_1 = p_1v_1$. Likewise, $F_2x_2 = p_2Ox_2 = p_2v_2$. After this process the work done on the gas is p_1v_1 and that done by it is p_2v_2. If the initial internal energy in A per unit mass of gas was U_1 and the final internal energy of the gas per unit mass of gas in B was U_2, then, by the law of conservation of energy, the energy change per unit mass of gas is given by

$$Q = -U_1 + U_2 - p_1v_1 + p_2v_2.$$

The convention of signs used in this equation, and in what follows, makes the work done *by* the gas *positive* and that done *on* the gas *negative*. U_2 is greater than U_1, for the gas has gained internal energy, and $U_2 - U_1$ is positive, for it is the work done by the gas in expanding against its internal pressure. It now becomes necessary to evaluate U_1, U_2, p_1v_1, and p_2v_2 by the use of Van der Waals' equation for a real gas.

$$U_2 - U_1 = \int_{v_1}^{v_2} p'dv = \int_{v_1}^{v_2} \frac{a}{v^2}dv = -a\left(\frac{1}{v_2} - \frac{1}{v_1}\right).$$

Writing the equation for the gas in AE and EB,

$$\left(p_1 + \frac{a}{v_1^2}\right)(v_1 - b) = RT_1$$

and

$$\left(p_2 + \frac{a}{v_2^2}\right)(v_2 - b) = RT_2.$$

Hence

$$p_1v_1 + \frac{a}{v_1} - bp_1 - \frac{ab}{v_1^2} = RT_1$$

and

$$p_2v_2 + \frac{a}{v_2} - bp_2 - \frac{ab}{v_2^2} = RT_2.$$

Combining these to get $p_2v_2 - p_1v_1$,

$$p_2v_2 - p_1v_1 = -\left(\frac{a}{v_2} - \frac{a}{v_1}\right) + b(p_2 - p_1) + ab\left(\frac{1}{v_2^2} - \frac{1}{v_1^2}\right) + R(T_2 - T_1).$$

Now ab is a small quantity of the second order, and so may be neglected. The expression for Q then becomes

$$Q = U_2 - U_1 + p_2v_2 - p_1v_1 = -2a\left(\frac{1}{v_2} - \frac{1}{v_1}\right) + b(p_2 - p_1) - R(T_1 - T_2).$$

To reduce the expressions in v into terms of p for practical use in the equation, the *ideal* gas relation $pv = RT$ may be utilized, for $1/v_2 - 1/v_1$ is a difference of the first order. An ideal gas differs from these by one part in a thousand or so. The error introduced in the difference between these two quantities expressed in terms of the pressure would be made one-tenth of 1 per cent by neglect of the corrections, since both v_1 and v_2 are volumes differing by a large amount. Thus $v_2 = RT_2/p_2$, and $v_1 = RT_1/p_1$ and the expression $2a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$ becomes

$$2a\left(\frac{p_2}{RT_2} - \frac{p_1}{RT_1}\right) = \frac{2a}{R}\left(\frac{T_1p_2 - T_2p_1}{T_2T_1}\right).$$

Now T_1 and T_2 differ by only a minute amount, as the early experiments of Gay-Lussac and Joule showed. In fact, $T_1 - T_2$ is of the order of 0.2°C. The factors multiplying p_2 and p_1 are of the order

$$\frac{273.2p_2 - 273.0p_1}{(273.2)(273.0)}.$$

An error of less than one-tenth of 1 per cent would be introduced in this quantity by writing this $(p_2 - p_1)/T$, where T could be chosen as the average value between T_1 and T_2. Thus

$$a\left(\frac{1}{v_2} - \frac{1}{v_1}\right) = \frac{a}{RT}(p_2 - p_1).$$

Therefore Q is given by

$$Q = -\frac{2a}{RT}(p_2 - p_1) + b(p_2 - p_1) - R(T_1 - T_2) = \left(\frac{2a}{RT} - b\right)(p_1 - p_2) - R(T_1 - T_2).$$

Now per unit mass of gas $Q = JC_v(T_1 - T_2)$, where J is the mechanical equivalent of heat and C_v is the specific heat at constant volume. Thus each unit mass of gas which goes from AE to EB is cooled or heated by $T_1 - T_2$, and, as it has a specific heat C_v, the heat consumed in raising that mass from T_1 to T_2 is $(T_1 - T_2)C_v$. Since the right-hand side of the equation is in work units, Q must be multiplied by J to make the equation uniform. Also an ideal gas has $C_p - C_v = R/J$, and in this experiment, since the gas is expanding, it is C_p which is needed. The error produced by using this approximation is negligible, for the heat consumed in overcoming molecular forces is small compared to the external work involved. Accordingly, the equation can have Q replaced by $Q = JC_v(T_1 - T_2) = -\frac{R}{J}(J)(T_1 - T_2) + JC_p(T_1 - T_2)$
and one obtains

$$-R(T_1 - T_2) + JC_p(T_1 - T_2) = \left(\frac{2a}{RT} - b\right)(p_1 - p_2) - R(T_1 - T_2)$$

or $$JC_p(T_1 - T_2) = \left(\frac{2a}{RT} - b\right)(p_1 - p_2),$$

that is, $$\frac{\Delta T}{\Delta p} = \frac{T_1 - T_2}{p_1 - p_2} = \frac{1}{JC_p}\left(\frac{2a}{RT} - b\right).$$

This equation says that if the gas in AE at a pressure p_1 be allowed to expand against a pressure p_2 in EB there will be a difference of temperature $T_1 - T_2$ set up on the two sides of E whose value is given by $\frac{1}{JC_p}\left(\frac{2a}{RT} - b\right)$, where a and b are the

Van der Waals constants, T is the absolute temperature, R the gas constant referred to the units in which a and b are expressed, C_p is the specific heat at constant pressure, and J is the mechanical equivalent of heat.

It is now of interest to discuss this result. According to the equation, the difference in temperature should be directly proportional to the difference in pressure. For pressure ranges which are not too great, this holds quite well. For higher pressures, the neglect of some of the terms in the derivation lead to a disagreement which is taken care of in a more perfect equation to be studied later. Furthermore, it should vary with $1/C_p$, which is not surprising, for the higher C_p the less the rise in temperature produced by a given amount of work. If $2a/RT$ is greater than b the gas should be cooled, for $T_1 - T_2$ will be positive, indicating that T_1 is greater than T_2. For some gases where b is larger than a, one obtains $T_1 - T_2$ negative, that is, a heating of the gas. It is obvious also that for high values of RT the $2a/RT$ will be less than b. Hence the effect should show a reversal in sign on reaching a certain temperature. The value of T for this reversal (the inversion temperature T_i) is given by setting

$$\frac{2a}{RT_i} = b \text{ or } T_i = \frac{2a}{Rb}.$$

These conclusions may now be tested by comparison with experiment. Since a and b are usually expressed in $cm^6 \times$ atmospheres and cm^3, it is necessary to transform the equation to the proper units. C_p, which is given per gram of gas, must be multiplied by ρ, the density of the gas. J, which is in ergs, must be converted into $cm^3 \times$ atmospheres by division by 1.013×10^6. R is in this case $1/273$ for $RT_0 = 1$ when $p = 1$ atm. and $v = 1$ cm^3. The equation then is

$$\frac{\Delta T}{\Delta p} = \frac{T_1 - T_2}{p_1 - p_2} = \frac{0.0242}{\rho C_p}\left(\frac{2a}{\frac{T}{273}} - b\right).$$

For CO_2, $a = 0.00874$, $b = 0.0023$, Van der Waals' values for Regnault's data taken at low pressures, comparable with the experiments for ΔT of Joule.

$$\rho C_p = 0.000399, \; T = 273.$$

Therefore $\Delta T/\Delta p = 0.925$; Joule observed $\Delta T/\Delta p = 1.05$.

For air, taking $a = 0.00257$ and $b = 0.00156$ from critical data, using $C_p = 0.000307$ and $T = 273$, one obtains $\Delta T/\Delta p = 0.274$, Joule observed a mean $\Delta T/\Delta p$ of 0.259 with values ranging from 0.244 to 0.288. For H_2 gas in which b is greater than a, using more recent values for a and b given by Jellinek,[12] and transformed to fit the equation as here given, one has $a = 0.00038$, $b = 0.001025$, $C_p = 0.000305$, and $T = 273°$abs. These give

$$\frac{\Delta T}{\Delta p} = \frac{(T_1 - T_2)}{(p_1 - p_2)} = -\underline{0.029}.$$

Joule observed a value of $\Delta T/\Delta p = -\underline{0.039}$, that is, the gas was *heated* on the side EB by an amount equal to 0.03°C. above the side AE per atmosphere pressure difference.

From the values for a and b the inversion temperature T_i of this heating effect can be estimated for H_2.

$$T_i = \frac{2a}{Rb} \text{ or } T_i = \frac{2a}{b} 273°\text{abs.}$$

$$T_i = \frac{0.00076}{0.001025} 273° = 202°\text{abs., or } -71°\text{C.}$$

Hence, at −71°C. the heating effect in hydrogen should change to a cooling effect. Actually, Olszewski[12] found a reversal at −80.5°C.

All these results show that, in general, there is agreement between the observed and theoretical values. Again, as in the critical constants, the effect depends on differences of small variable quantities. Thus the numerical agreement is not entirely satisfactory. Further errors are introduced by the simplifying assumptions used. A careful thermodynamic treatment of the case, for which the reader is referred to Jellinek,[13] gives the more exact result that

$$\frac{dT}{dp} = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p}.$$

Writing Van der Waals' equation in the form

$$v = \frac{RT}{p} - \frac{a}{pv} + \frac{ab}{pv^2} + b$$

and simplifying it by replacing pv by RT,

$$v = \frac{RT}{p} - \frac{a}{RT} + \frac{abp}{R^2T^2} + b$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2} - \frac{2abp}{R^2T^3}$$

and

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = \frac{2a}{RT} - \frac{3abp}{R^2T^2} - b.$$

Thus

$$\frac{dT}{dp} = \left(\frac{2a}{RT} - \frac{3abp}{R^2T^2} - b\right)\frac{1}{JC_p}.$$

This differs from the former equation in that it has the negative term $\frac{3abp}{R^2T^2}$ in it. Thus for large values of p, dT/dp should decrease with increasing pressure, as it is observed to do. dT/dp becomes zero for the condition that $\frac{2a}{RT} - \frac{3abp}{R^2T^2} - b = 0$. This is a quadratic equation in T and there are thus two temperatures at a given pressure at which the effect disappears. This makes the pressure-temperature curve for the disappearance of the Joule-Thomson effect a parabola, and its course is more complicated than the simple theory which holds only for low pressures.

The Joule-Thomson effect is used in determining that temperature on the centigrade scale which represents the absolute zero of temperature. The method is, however, thermodynamical and finds no place in this text.

54. Other Equations of State.[28]—As has been seen, Van der Waals' equation is but a first-order approximation. Its imperfections have spurred various workers on to improve its agreement with experiment. In studying the improvements proposed, one might, with Jeans,[14] use two deviations as criteria in discussing the equations. It was found in Sec. 52 that $v_c = 3b$ for gases from Van der Waals' equation. In general, v_c is more nearly $2b$. Also it should follow from the theoretical values of p_c, v_c, and T_c that $p_cv_c = \frac{3}{8}RT_c$. Actually, RT_c is more nearly 3.7 p_cv_c than 2.66 p_cv_c as the theory demands.

It is possible to write Van der Waals' equation in another form known as the *reduced equation of state*. If for the variables p, v, and T one substitute the variables P, V, and T_1 related to p, v, and T by $T_1 = T/T_c$, $P = p/p_c$, $V = v/v_c$, then, from the

values of the critical constants (Sec. 52), one obtains Van der Waals' equation in the form

$$\left(P + \frac{3}{V^2}\right)\left(V - \frac{1}{3}\right) = \frac{8}{3}T_1.$$

This equation is the same for all gases, for the characteristic constants a and b have been eliminated. It is merely necessary to find p_c, v_c, and T_c to express the equation in the reduced form.

There are two ways in which the improvements of Van der Waals' equation have been attempted. The first is by means of added constants of an empirical nature. The second is by the more rigorous deduction of the equation allowing for temperature and other variations of a and b.

With the relations above in mind, one may go to a typical attempt to modify Van der Waals' equation to agree with facts more closely by the use of empirical relations. Kammerlingh-Onnes[18] uses a quantity K defined by the relation $K = RT_c/p_cv_c$, which characterizes the deviation from Van der Waals' equation as suggested above. This K is dimensionally a pure number. Calling $V_k = V/K$ the Van der Waals equation above in this new notation reduces to

$$\left(P + \frac{27}{64V_K^2}\right)\left(V_K - \frac{1}{8}\right) = T_1.$$

This can be transformed into

$$PV_K = \frac{T_1}{1 - \dfrac{1}{8V_K}} - \frac{27}{64V_K},$$

which expands into

$$PV_K = T_1\left\{1 + \frac{1}{V_K}\left(\frac{1}{8} - \frac{27}{64}\frac{1}{T_1}\right) + \frac{1}{64V_K^2} + \frac{1}{512V_K^3} + \cdots\right\}.$$

This equation is, however, not satisfactory even when the experimental value of K has been introduced, for it was seen that it was not only the position of the theoretical isotherms but their actual shapes which deviated from the observed ones. In other words, making the critical isotherm agree in one point with experiment did not insure agreement of the other isotherms. Kammerlingh-Onnes *assumed* a purely empirical form of the equation above and wrote it

$$PV_K = T_1\left(1 + \frac{B}{V_K} + \frac{C}{V_K{}^2} + \frac{D}{V_K{}^4} + \frac{E}{V_K{}^6} + \frac{F}{V_K{}^8}\right)$$

where B, C, D are themselves series of the form

$$B = b_1 + \frac{b_2}{T_1} + \frac{b_3}{T_1{}^2} + \frac{b_4}{T_1{}^3} + \frac{b_5}{T_1{}^4} + \ . \ . \ .$$

This gives at least 25 adjustable constants. Such an equation has no basis in theory. With that many constants it should be possible to obtain close agreement with any observed curve. For a discussion of the success of this equation one may be referred to Jeans.[14] It serves as an example of one of the most successful attempts at an accurate empirical representation.

Clausius[15] attempted an empirical modification of Van der Waals' equation. This takes the form

$$\left(p + \frac{a'}{T(v + c)^2}\right)(v - b) = RT.$$

He introduces in place of the old constant a a new constant a', which is divided by the absolute temperature. Thus he makes the old a inversely proportional to the absolute temperature. Besides this, an adjustable constant c is added to the v in the expression for the internal pressure of Van der Waals. The introduction of a temperature correction into a is not quite empirical, for a is theoretically expected to depend on temperature. This correction alone improves the fit of Van der Waals' equation to the data leaving c out. Better agreement is obtained for a properly chosen c. The formula fits Andrews' results in CO_2 better than the original equation at high densities; at low densities it gives a poorer fit. For other gases it is even less successful. Clausius then devised a still more elastic equation containing one more constant and putting an undetermined exponent on the temperature correction. This gave better fits for some gases, as was to be expected, but again failed when extended to more gases. Thus it appears that the agreements of empirical equations obtained by extending Van der Waals' equation can, by choosing enough constants, be made to fit experimental data more or less accurately. They, however, teach nothing about the phenomena and do not suggest further investigation. They serve a useful purpose in expressing the true behavior of a gas in a condensed and serviceable form which

permits of the introduction of such accurate relations into applications demanding the relations which they yield.

An attempt at a theoretical improvement of the equation of state applicable to limited ranges of volume has met with a success that merits discussion. This attempt results in an equation first empirically proposed by Dieterici which has been placed on a rigorous theoretical basis by Jeans.[16] The latter deduces this equation from a generalized calculation of the gaseous pressure. This general expression for the pressure is of an exceedingly complex character, involving the molecular densities due to different conditions existing. Jeans evaluates the expression for the gas pressure, assuming spherical molecules having a definite diameter σ. He allows for the existence of forces of cohesion, the method of attack involving a study of the changes in molecular densities at and near the surface of the gas produced by these forces. Making certain approximations he arrives at the expression $p = \frac{RT}{v - b} e^{-\frac{a}{RTv}}$ which is Dieterici's equation. It is seen that it is the same as Van der Waals' equation except that the $p + a/v^2$ is now replaced by $pe^{\frac{a}{RTv}}$. This equation gives Van der Waals' equation when a and b are small. Theoretically, as Jean points out, this equation has a range of validity no better than Van der Waals' equation at great pressures. It gives for v_c, however, a theoretical value of $2b$, which is more nearly in accord with experiment, while $K = \frac{RT_c}{p_c v_c} = \frac{1}{2}e^2$, or 3.695, which fits the experimental values more closely than does the value 2.66 from the original equation of Van der Waals. In fact, it was to obtain these numerical relations that Dieterici set up his original equation, this equation being the best of several proposed. It agrees well with the data for isopentane for pressures less than 12 atm. and holds fairly well beyond this range. In general, it is numerically slightly more satisfactory than the original Van der Waals equation, although it is far from correct.

It is seen that with increasing experimental accuracy the difficulty of finding any one equation of state for real gases becomes exceedingly great. Van der Waals' original equation with its constant coefficients a and b is but a second-order approximation. Attempts such as those of D. Berthellot, Dieterici, and Reinganum, making a and b functions of T, offer

some improvement. Here again difficulty is encountered in giving a universally proper form to the functions, for the form giving a satisfactory result for one gas does not give such a result for another gas. This merely means that each gas has different laws of force between its atoms or molecules, so that general equations become unserviceable for the case of individual gases in precise studies. In discussing such laws of force, it was found that in general a law of the form $\phi(r) = Dr^{-m} - Gr^{-n}$ sufficed to a first approximation with the first member the attractive term, and the second member the repulsive term, the latter being perhaps more accurately of the form $a_1 e^{-\lambda r}$, where a_1 and λ were constants. In applications of this law to individual gases, the exponents m and n need to be determined for each gas. Obviously the immediate task of finding the proper equation of state for a given gas to a first order resolves itself into the problem of evaluating m and n for the individual gases. To solve this problem, one may find aid in the empirical equations which yield accurate agreement with experiment.

When one turns to purely empirical expressions, the equation of Kammerlingh-Onnes which for this discussion may be written as

$$pv = A_v + \frac{B_v}{v} + \frac{C_v}{v^2} + \frac{D_v}{v^4} + \frac{E_v}{v^6} + \frac{F_v}{v^8}$$

is completely satisfactory for describing the behavior of any gas as accurately as experiment yields it. In this equation the coefficients A_v, B_v, . . . are functions of T, and, for reasons that will soon become clear, they are termed respectively the first, second, . . . virial coefficients. While such an equation is of use, it is unsatisfactory because it is quite empirical. As a result of the initial work of Kammerlingh-Onnes[21] and later Keesom,[22] Holborn and Otto,[23] and finally Lennard-Jones,[24] it has been possible to relate this empirical expression in certain parts to the theoretical expressions deduced for the equation of state. As a result of this interrelation it has been possible to arrive at a *semi-empirical* equation of state which enables one, from the experimental values of the constants for the second virial coefficient in Kammerlingh-Onnes equation, to infer the coefficients of the attractive- and repulsive-force laws of any gas to a first degree of approximation.

In order to study this question, one may rewrite the simple Van der Waals equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

in an expanded form obtained through division by $v - b$, as

$$pv = RT + \frac{RTb - a}{v} + \frac{RTb^2}{v^2} + \cdots$$

In this equation the terms a and b were assumed constant. As shown by the deduction of Reinganum's equation, however, both a and b are functions of T. Hence one should more properly express this relation in the form

$$pv = RT - \frac{f(T)}{v} + O\left(\frac{1}{v^2}\right).$$

Fowler[25] has shown that from the theorem of the virial the real gas law for moderate pressures is given in a general form by the equation

$$pv = NkT\left[1 - 2\pi\frac{N}{v}\int_0^\infty r^2\left(e^{-\frac{E}{kT}} - 1\right)dr\right].$$

In this equation, $Nk = R$; and E is defined as the potential energy of the molecules at a distance r. Thus $\phi(r) = -\frac{dE}{dr} = Dr^{-m} - Gr^{-n}$, if the repulsive-attractive forces as suggested above are used. It is seen at once that the second term, $\frac{RTb - a}{v} = \frac{-f(T)}{v}$, is equivalent to the term $-\frac{2\pi RT}{v}N\int_0^\infty r^2(e^{-E/kT} - 1)dr$. This last term comes from the second virial in the deduction of the gas law, whence from its relation to B_v the latter can be termed the second virial coefficient. Writing the Fowler expression beside the Kammerlingh-Onnes equation

$$pv = RT - \frac{2\pi RTN}{v}\int_0^\infty r^2\left(e^{-\frac{E}{kT}} - 1\right)dr$$

$$pv = A_v + \frac{B_v}{v} + \cdots,$$

one observes at once that the second virial coefficient can be readily related to the force integral by the expression

$$\frac{1}{N}\frac{B_v}{A_v} = 2\pi\int_0^\infty r^2\left(1 - e^{-\frac{E}{kT}}\right)dr$$
$$= \frac{2\pi}{3kT}\int_0^\infty r^3\left(-\frac{dE}{dr}e^{-\frac{E}{kT}}\right)dr.$$

Hence, if one assumes some general law of force $\phi(r) = -\frac{dE}{dr} = Dr^{-m} - Gr^{-n}$, it is possible to evaluate D, G, m, and n from the variation of $\frac{1}{N}\frac{B_v}{A_v}$ with temperature. It is of importance to note that, if $\frac{1}{N}\frac{B_v}{A_v}$ is to remain finite with the law assumed, m and n must both be greater than 4, a point of some importance, previously mentioned. Assuming this relation, it is shown by Fowler[26] how the complex equations obtained by inserting the expression for E as a function of r into the relation above can be solved for the constants. The solution is simplified by a graphical procedure which enables the most suitable combinations of values of m and n to be chosen for a given set of observed values of B_v/A_v plotted against log T. Having chosen m and n, the constants D and G can readily be determined. As may be imagined from the magnitude of the exponents used and the relatively low range in values of T, the decision as to the most suitable combination of exponents is not very simple nor is it unambiguous. In addition, the number of gases for which complete data are available is very limited. Kammerlingh-Onnes and, later, Holborn and Otto have, for the inert gases, reduced the observational material to a suitable form for analysis. Where these data overlap, they are fairly consistent except at the lower temperatures. The nature of the results obtained from the more self-consistent data of Holborn and Otto are shown on page 198.

The study of the repulsive forces is also possible by an analysis of the viscosity (see Sec. 62) thanks to the analyses of Chapman and of Enskog.[27] Assuming vanishingly small attractive forces, it is possible from the temperature variation of viscosity to evaluate the exponent n in a repulsive law, assuming $f(r) = Gr^{-n}$ and an attractive law of the inverse-cube type. This law has given values for n in close agreement with those from the equation of state for He and H_2 where the attractive forces are very feeble. The comparison of the computed values for n

from (1) the equation of state and (2) the viscosity data are given in the table on page 199, together with the "diameters" of the molecules computed from the data. The numbers in boldfaced type indicate the values that have been selected from these results together with data from other sources as the most suitable values, since, as seen above, these data alone do not give a unique solution.

THE FORCE CONSTANTS OF GASES (D AND G) FROM THE EQUATION OF STATE
The figures in brackets are the "diameters" in Ångström units

Gas	$n = 9, m = 5$		$n = 11, m = 5$		$n = 14\frac{1}{3}$,* $m = 5$		$n = \infty, m = 5$	
	$D \times 10^{74}$	$G \times 10^{45}$	$D \times 10^{90}$	$G \times 10^{45}$	$D \times 10^{115}$	$G \times 10^{45}$	σ	$G \times 10^{45}$
Helium.....	1.31 (4.10)	5.25	6.97 (3.57)	3.56	2.35 (3.12)	2.33		
Neon.....	6.32 (4.99)	22.3	43.8 (4.29)	17.2	22.2 (3.70)	13.3	..... (2.42)	7.3
Argon.....	101.0 (7.05)	162.0	1,310.0 (6.03)	138.0	1,640.0 (5.11)	113.0	..... (3.13)	70.4
Hydrogen....	9.19 (5.23)	25.4	73.8 (4.52)	19.8	48.9 (3.92)	15.6	..... (2.59)	8.5
Nitrogen.....	158.2 (7.46)	182.0	2,245.0 (6.36)	151.0	3,610.0 (5.42)	123.0	..... (3.38)	77.0

* This fractional number has advantages in the numerical work.

It is seen that repulsive forces of the inverse fourteenth power appear to give the best results for He, while for Ne it is the inverse eleventh, for argon the inverse ninth, and for H_2 the inverse eleventh power. The values used for m, the attractive force, at the time these tables were compiled, is the inverse-fifth-power law. It now seems probable that this is not correct and that the attractive forces of an inverse-sixth-power type are more likely. Until greater experimental accuracy can be achieved, these values must, however, suffice. In any case, despite the uncertainties discovered, it is quite clear that the semi-empirical procedure has materially aided in the advance of understanding of the problem and leaves the question one of finding the appropriate laws of force appertaining to each individual molecular species in the measure that advances in experimental technique permit.

REPULSIVE-FORCE CONSTANTS AND "DIAMETERS" (IN PARENTHESES) OF ATOMS AND MOLECULES OF GASES* IN ÅNGSTRÖM UNITS

Gas	Method	$n = 9$	$n = 11$	$n = 14$	$n = 14\frac{1}{3}$	$n = 15$	$n = 21$	∞
He	(1)	1.31×10^{-74} (4.10)	6.97×10^{-90} (3.57)	.....	2.35×10^{-115} (3.12)			
	(2)	.....	.....	$\mathbf{5.74\times10^{-113}}$ (3.12)				
Ne	(1)	6.32×10^{-74} (4.99)	$\mathbf{4.38\times10^{-89}}$ (4.29)	.....	2.22×10^{-114} (3.70)	.....	.....	..... (2.42)
	(2)	6.66×10^{-74} (5.02)	4.45×10^{-89} (4.30)	.....	.....	1.76×10^{-119} (3.60)	3.89×10^{-165} (3.153)	..... (2.35)
Ar	(1)	$\mathbf{1.01\times10^{-72}}$ (7.05)	1.31×10^{-87} (6.03)	.....	1.64×10^{-112} (5.11)	.....	2.34×10^{-162} (4.34)	..... (3.13)
	(2)	.....	3.92×10^{-88} (5.35)	.....	3.57×10^{-113} (4.70)	.....	2.82×10^{-163} (3.99)	..... (2.84)
		($n = 10$)						
Kr	...	$\mathbf{7.34\times10^{-80}}$ (6.98)						
Xe	...	.....	$\mathbf{6.21\times10^{-87}}$ (7.05)					
H_2	(1)	9.19×10^{-74} (5.23)	$\mathbf{7.38\times10^{-89}}$ (4.52)	.....	4.89×10^{-114} (3.92)	.....	.....	..... (2.59)
	(2)	.....	$\mathbf{7.19\times10^{-89}}$ (4.51)					
N_2	(1)	15.82×10^{-73} (7.46)	22.45×10^{-88} (6.36)	.....	3.61×10^{-112} (5.42)	.....	.....	..... (3.38)
	(2)	7.59×10^{-73} (6.81)	9.08×10^{-88} (5.81)	.....	.....	1.17×10^{-117} (4.84)	.....	..... (3.15)

(1) From equation of state.

(2) From viscosity.

* This and the preceding table are reproduced with the permission of R. H. Fowler from his admirable text "Statistical Mechanics."

References

1. MEYER, O. E.: "Kinetic Theory of Gases," 2d ed., Appendix, part III, Par. 34, p. 77, Maruschke und Berendt, Breslau, 1899; English edition, translated by Baynes, Mathematical Appendix, p. 423, Longmans, Green & Co., London, 1899.
2. CLAUSIUS, R.: "Die Kinetische Theorie der Gase," Chap. II, Sec. 5, p. 57, F. Vieweg und Sohn, Braunschweig, 1889.
3. JAEGER, G.: *Sitzb. Akad. Wiss. Wien*, **105** (2*A*), 111 (last page), 1896.
4. JELLINEK, K.. "Lehrbuch der Physikalischen Chemie," vol. 1, part I, p. 379 ff., F. Enke, Stuttgart, 1914.
5. JAEGER, G.: "Die Fortschritte der Kinetischen Gas Theorie," p. 54, F. Vieweg und Sohn, Braunschweig, 1919.
6. CLAUSIUS, R.: *Ann. Physik*, **2**, 124, 141, 1870. Also *loc. cit.*, pp. 60–65.

7. Clemens-Schaefer: "Einführung in die Theoretische Physik," vol. 2, part I, Sec. 78, p. 331, Vereinigung Wissenschaftlichen Verleger, Berlin, 1921.
8. Lorentz, H. A.: *Ann. Physik*, **12**, 127, 660, 1881.
9. Jellinek, K.: *Loc. cit.*, vol. 1, part I, p. 391.
10. Hertzfeld, K. F.: "Handhuch der Physik," vol. 22, Chap. 5, Secs. B, C, F, and G. Edited by H. Geiger and K. Scheel, Julius Springer, Berlin, 1926.
11. Fowler, R. H.: "Statistical Mechanics," p. 214, Cambridge University Press, Cambridge, 1929.
12. Jellinek, K.: *Loc. cit.*, vol. 1, part I, p. 408.
13. Jellinek, K.: *Loc. cit.*, vol. 1, part I, p. 400.
14. Jeans, J. H.: "Dynamical Theory of Gases," Chap. VI, Sec. 190, p. 148, Cambridge University Press, Cambridge, 1921.
15. Clausius, R.: *Ann. Physik*, **9**, 387, 1880.
16. Jeans, J. H.: *Loc. cit.*, Chap. VI, Sec. 206, p. 161.
17. Reinganum: See Jellinek: *Loc. cit.*, vol. 2, part XXIII, Chap. IV, p. 158. Jaeger, G.: *Loc. cit.*, Chap. IV, p. 85.
18. Kammerlingh-Onnes: *Arch. Néerland Sci.*, **6** (2), 874, 1901.
19. Fowler, R. H.: *Loc. cit.*, p. 215ff.
20. Fowler, R. H.: *Loc. cit.*, Table 17, p. 227, Table 20, p. 234.
21. Kammerlingh-Onnes: *Comm. Phys. Lab. Leiden*, No. 71, 1902.
22. Keesom: *Comm. Phys. Lab. Leiden, Suppl.* 24*B*, p. 32, 1912.
23. Holborn and Otto: *Z. Physik*, **23**, 77; **30**, 320, 1924; **33**, 1, 1925; **38**, 359, 1926.
24. Lennard-Jones: *Proc. Roy. Soc.*, **A106**, 463, 1924.
25. Fowler, R. H.: *Loc. cit.*, p. 211ff.
26. Fowler, R. H.: *Loc. cit.*, p. 221ff.
27. Fowler, R. H.: *Loc. cit.*, p. 229ff.
28. Van der Waals, J. D., Jr.: "Handbuch der Physik," vol. 10, Chap. III, pp. 126–161, Geiger and Scheel; Julius Springer, Berlin, 1926.

Books Recommended

a. Jellinek, K.: *Loc. cit.*, vol. 1, parts I and II, Sec. $A\alpha$ 3 and 5, and $A\gamma$ 1 and 2; Chaps. I, II, III, IV. Admirable in completeness; contains all references.
b. Clemens-Schaefer: *Loc. cit.*, Chap. VIII, Secs. 78, 88. An excellent mathematical treatment of the theorem of the virial.
c. Jeans, J. H.: *Loc. cit.*, Chap. VI, Sec. 161ff. Gives an admirable summary of present state of subject; comparison of theories and literature.
d. Fowler, R. H.: "Statistical Mechanics," Chaps. IX, X, Cambridge University Press, Cambridge, 1929.
e. Van der Waals, J. D., Jr.: "Handbuch der Physik," vol. 10, Chap. III, pp. 126–161, Geiger and Scheel, Julius Springer, Berlin, 1926.

CHAPTER VI

TRANSFER OF MOMENTUM, TRANSFER OF ENERGY, TRANSFER OF MASS THROUGH A GAS. THE KINETIC THEORY OF THE COEFFICIENTS OF VISCOSITY, HEAT CONDUCTION, AND DIFFUSION

55. Introduction.—In Chap. III it was shown that, in spite of their high speeds, gas molecules liberated at one point in a space did not instantaneously appear at points at moderate distances from the origin. The reason for this was shown to be due to the effect of collisions with the myriads of molecules present in unit volume which prevented a molecule traveling for more than a very short distance in any given direction. This led at once to the concept of the mean free path, which was discussed in detail in that chapter. The correctness of this concept was there demonstrated by direct measurements of the mean free path and distribution of free paths all of more or less recent date. When the kinetic theory was developing, the experimental technique and the knowledge in such fields as electronics had not developed to the extent necessary to permit these verifications. In fact, no direct test of the mean-free-path concept was then possible. In attempting to demonstrate the correctness of the hypothesis, it was natural that the workers should have turned for its verification to the striking discrepancy with the notion of rapidly moving molecules (*i.e.*, the slow diffusion and heat transfer) which had led to the mean-free-path concept. Thus at a very early date the three phenomena depending on molecular velocities and free paths which could throw light on the low values of the latter were carefully analyzed. These three phenomena depend on the transfer of matter, of momentum, and of energy through a gas. They lead in an experimental study to three constants depending on the nature of the gas, called the coefficients of diffusion, viscosity, and heat conduction.

The analysis of these three constants from the kinetic-theory point of view led to predicted variations of the constants with pressure, temperature, and masses of the molecules. Some of these variations were at the time unknown. Their verification

afforded a striking proof of the correctness of the assumptions involved. They also led to predicted relations between the coefficients of heat conduction and viscosity, which were found to be approximately correct. Some of the predictions, notably the temperature variations, were not fulfilled. Where this was the case, it was found that the theoretical simplifications and some of the assumptions (*e.g.*, that of forceless molecules of fixed diameters) were not strictly true, and that to this extent the theory had to be modified.

The deductions also led to relations which enabled the mean free paths of the molecules L to be evaluated. These values are in excellent agreement in order of magnitude with those estimated from the Van der Waals equation (Chap. V) and from the more direct measurements of Chap. III. The lack of complete numerical agreement must be ascribed to two causes: first, to the fact that, as the free path L is a function of the temperature, the results of the measurements are not strictly comparable; and second, to the uncertainty as to the value of the numerical constants resulting from differences in the manner of averaging the velocities (*e.g.*, the Maxwell and Tait free paths (Sec. 39) or Jeans' persistence of velocities).[1] At the time, however, the agreement between theory and experiment was most striking, and today, in spite of the more complicated analysis necessary for a satisfactory treatment, the study of these coefficients in the light of the kinetic theory furnishes an inspiring example of this type of analysis. It is the purpose of this chapter to give both the elementary treatment of the problems and some of the later, more accurate findings. For the proper treatment of the subject, it seems best to derive the expressions in an order which places the coefficient of viscosity first, heat conduction second, and diffusion last, because of the relative mathematical simplicity of the cases of viscosity and heat conduction compared to diffusion. The chapter will be divided into three parts: Part I, Coefficient of Viscosity; Part II, Coefficient of Heat Conduction; Part III, Coefficient of Diffusion.

56. Irreversible Phenomena.—Before proceeding to a discussion of Parts I, II, and III, it is of interest to point out a marked difference in the case of these phenomena compared to the phenomena which formed the basis of the discussions of all previous chapters. In those chapters the discussion was limited

chiefly to the cases of gases in equilibrium. In such cases the temperature and the partial pressure of the gases remained constant throughout. In fact, the deductions of Chap. IV depended on this equilibrium. Thus in the cases treated there was no streaming motion in the gas and one part of the gas was like another part as regards constitution, momentum, and energy distribution. Part I and the following parts deal with gases which are not in equilibrium and which are striving to attain that state.

It is a fact of common experience that, if a gas is set in motion in its container, the motion will be gradually dissipated until the temperature and the pressure of the gas are uniform throughout and there is no directly observable motion in the gas. The phenomenon of the dissipation of internal motion is known as "viscosity." It is perhaps the simplest of the irreversible phenomena.

Again, if the gas in a container is not at a uniform temperature throughout, differences of density arise, and so, owing to the buoyant action arising from gravitational force and governed by Archimedes' principle, convection currents arise. These motions are dissipated by viscous friction, and so, ultimately, temperature equilibrium is attained. But there is a more direct process by which the temperature equilibration is carried out, and which is present in arrangements where convectional streaming is prevented. This process is that of heat conduction.

The third principal irreversible phenomenon is that of diffusion. In this a gas consisting of a mixture of different varieties, the composition of which is initially variable from point to point, gradually becomes uniform. As different gases do not have the same density at the same temperature and pressure, there is also convective action which results in mixing when the gas is, as is usually the case, in a gravitational field. The phenomenon of diffusion, properly speaking, is, however, one which takes place independently of this convective action. It is due, as are the other two real processes, viscosity and heat conduction, to the eternal and chaotic random heat motions of the molecules.

The designation "irreversible" for these phenomena arises from the fact that all three are conditioned by the second law of thermodynamics, being processes in which the energy is degraded (*i.e.*, in which the molecular chaos ("mixed-upness") of the

universe is increased). It is important to note that the second law of thermodynamics tells merely the *direction* of the phenomena—that is, that the streaming motions will be dissipated, that the temperature will become uniform, and that the composition will become uniform. Thermodynamics does not offer any information about the time rate, or speed, with which these processes take place. Experiment and the kinetic theory, by giving information about the time rates of these phenomena, thus make a great advance over the doctrine of energetics.

I. VISCOSITY

57. The Experimental Definition of Viscosity.—Consider a gas in a container having plane parallel walls infinite in extent. Assume, now, that one of these remains fixed while the other one moves relative to it with a velocity u. Let the distance between these two walls be z. An arrangement of this sort could be realized experimentally by having the moving wall a long, flat belt moving endlessly over two rollers, and considering a small region far from the rollers. Experiment has shown that the gas will be set in motion in the direction of the moving belt, that it will be at rest relative to each boundary, at the boundary (except for a slight slipping to be discussed later), and that the motion of the gas between the plates will fall off linearly from the moving plate to the fixed one—that is, the gas next the moving plate will be set into motion by it, momentum being lost by that plate in transmitting motion to the gas. The outer layer of gas will then set the next inner layer into motion, suffering thereby a loss of momentum, so that its velocity will be less than that of the plate. Thus a gradient of velocity will be set up across the gas space, which experiment shows is a linear one. If the velocity of the layer of gas at the plane $z = 0$ is designated as 0, and at $z = z_0$ as u_0, the rate of increase of speed with z, or the velocity gradient, is $\frac{u_0}{z_0}$. When the steady state of motion is reached, the upper plate is losing momentum to the gas, and as a result experiences a viscous force or drag which is equal to the rate of loss of momentum. Thus the viscous force of the gas is measured by the rate of change of momentum involved.

Experimentally, it was found that the force was proportional to the area of the moving plane exposed to the gas, and to the

velocity gradient in the gas. That is, if f be the force on the plane, A its area, and $\frac{du}{dz}$ the velocity gradient, then

$$f = -\eta A \frac{du}{dz},$$

and if F be the force per unit area,

$$\frac{f}{A} = F = -\eta \frac{du}{dz}.$$

Here η is a constant of proportionality characteristic of the gas, the coefficient of viscosity. The negative sign denotes that the force opposes the motion u. It is the significance of η in terms of the molecular quantities which it is desired to derive from the kinetic theory. In the c.g.s. system of units η gives the force in dynes per cm^2 acting on the surface when the velocity gradient is 1 cm/sec. in a cm taken normal to the surface, *i.e.*, along the z-axis. To orient oneself, it may be of interest to note that η for air is 1.8×10^{-4} dyne/cm^2 per unit gradient, while η for H_2 is 0.9×10^{-4}, η for water is 0.01 at 20°C., and η for glycerine is 8.5 at 20°C. In mentioning the value of η for liquids whose definition and experimental measurement are precisely the same as for those of gases, it becomes essential to point out a fundamental difference between the interpretation of η for the two classes of substances on the kinetic theory. In gases the intermolecular forces are considered as completely negligible, or at least relatively small, in their effects compared to the peculiar type of transfer assumed. In liquids, the intermolecular forces, as evidenced by cohesion, play an entirely dominating rôle. Hence viscosity in liquids is largely governed by cohesive forces and shows little dependence on density, molecular velocity, or mean free path. It is, therefore, not surprising that liquids whose cohesive forces rapidly become weakened as temperature increases should show *reduced viscosity* with *increasing* temperatures. In gases where, as will be seen, the viscosity depends on the rate of transfer of momentum, the viscosity *increases* as temperature increases.

58. The Simple Kinetic Analysis of Viscosity.—The first analysis of η from the point of view of the kinetic theory was due to Maxwell in 1860.[2] From the discussion of the previous section, it was evident that the viscous drag exerted by the gas on the plane was due to a loss of momentum of the plane to the gas. This transfer of momentum from the faster layer to the adjacent

slower layer was then found to take place throughout the gas, leading to the establishment of a velocity gradient from one plate to the next. It also leads to the manifestation of a viscous drag on the stationary plane which could be detected by a suitable measuring device, showing that some of the momentum of the moving plane is being transmitted through the gas to the fixed plane.

This transfer of momentum through the gas may be pictured by the kinetic theory in the following fashion: According to the distribution law, the molecules are moving in the gas in a completely random fashion with average velocity components equal along the three axes. The streaming motion of the gas merely indicates that there is a minute average additional velocity of all the molecules in the given directions. This additional velocity, a few cm/sec., is so small compared to C (about 40,000 cm/sec.) that it may be assumed to be of little influence on the Maxwellian law of distribution. If the velocity gradient exists in the gas, the molecules in one of the upper, more rapidly moving layers (that is, one having a small additional component u_1 in the x direction) will move from this layer to one of the lower and slower layers, carrying with it its initial component u_1 in the x direction. If in this lower layer where the speed of the molecules along the x direction is lower (*i.e.*, where the average velocity of the molecules in the x direction is $u_2 < u_1$) the first molecule suffers collision, its added momentum will be given up to the lower layer. Thus the lower layer will move faster as a result of this. On the other hand, some molecules from the lower layer will, by their heat motions end in the upper layer, and being slower, will decrease the average momentum of the molecules in the upper layer. It is then by such a process that the momentum is transferred from layer to layer of a gas and it is from a precise analysis of this process that it should be possible to derive the expression for η.

To this end the following simple assumptions may be made: Let it be assumed that an average molecule traverses a distance equal to the mean free path between impacts. The length of this path is then a rough measure of the thickness of the layer of gas in which viscous action occurs. On the two sides of a layer of gas L cm thick, whose plane is parallel to the plates, the difference of streaming velocity in the gas is given by $L \frac{du}{dz}$, for the

velocity gradient normal to the motion of the gas is $\frac{du}{dz}$. Thus molecules of mass m coming from the upper side of this layer to the lower side carry an excess of momentum $mL\frac{du}{dz}$ from the upper to the lower side. Now, on the average, one-third of the molecules are moving with paths that are up or down. Thus the number of molecules of speed $\bar{c}$ going up or down across unit area per second will be one-third $N\bar{c}$, where there are N molecules per cm^3. The momentum transferred across this layer up and down by the molecules is thus

$$\frac{1}{3}Nm\bar{c}L\frac{du}{dz}.$$

Now this calculation was made on the assumption of a uniform gradient. This presupposes a steady state.* That means that momentum is being passed on from one layer to the next as rapidly as it is received. Thus the transfer of momentum across the layer L is the same as that given to the gas by the moving plane at z_0 or given to the stationary plane at $z = 0$. This momentum transfer in the gas thus results in a force $-F$ being exerted on the moving plane at z_0, the reaction a force equal in magnitude but opposite in sense being exerted on the lower plane at $z = 0$, of magnitude $+F$. Hence

$$F = \frac{1}{3}Nm\bar{c}L\frac{du}{dz}.$$

By the definition of η, this force $F = \eta\frac{du}{dz}$ per unit area as regards the lower plate. Therefore

$$\eta = \frac{1}{3}Nm\bar{c}L.$$

This equation also follows in exactly the same form from a distinctly more rigorous deduction to be given in the following section. For a discussion of this expression for η as compared with experiment the reader is referred to Sec. 60 at the end of the deduction of this expression.

59. Maxwell's Deduction of the Value of η.—Assume a gas in which a uniform velocity gradient is set up by some adequate

* It is to be observed that by "equilibrium in a gas" is meant uniformity of temperature, velocity, and composition throughout the gas, whereas the term "steady state" merely means that the temperature, velocity, and composition *at a given point do not vary with time.* They may, however, vary from place to place.

experimental arrangement. Choose a point in the gas stream and set up a system of coordinate axes such that the gas moves along the x-axis with a velocity u_o, while the velocity gradient lies along the z-axis. Thus at $z = 0$, u will be u_o. As the velocity gradient is $\frac{du}{dz}$, the velocity at any point $z = z$ will be

$$u = u_o + \frac{du}{dz} z.$$

Owing to this gradient, the molecules which are continually moving from positive values of z through the xy plane are carrying with them momentum corresponding to the region where they

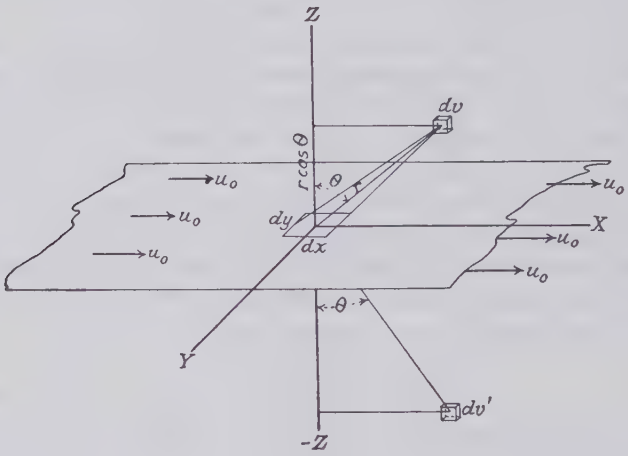

FIG. 38.

last suffered an impact. The validity of this assumption is questioned by Jeans[1] on the basis of his theorem of persistence of velocities. Similarly, the molecules moving from negative values of z are moving through the xy plane, transferring their low momenta along x to the upper layer and decreasing the average momentum of the layer. The net momentum transfer per unit time through unit area gives the force per unit area exerted due to the velocity gradient across the xy plane. To get this, one takes a small element of volume dv (Fig. 38) and finds the rate of transfer of momentum downward through a small area $dxdy$ due to this volume. The same may be done for the upward transfer of momentum through $dxdy$ due to a small volume dv' below the xy plane. By integrating these over all the space above and

below xy the *net* momentum transfer through $dxdy$ per second, and hence the force exerted, may be found.

Assume a small volume dv having N molecules per cm³ in it. Assume, further, that, on the average, a single molecule experiences $\bar{z}$ collisions in unit time. This quantity may, for purposes of simplification, be considered as $\frac{\bar{c}}{L}$, a constant, where $\bar{c}$ is the average velocity and L is the mean free path. As was seen in Sec. 39, this is really not the case, and in later work the accurate expression for the mean collision frequency will be used. In a time dt the Ndv molecules in dv experience $N\bar{z}\,dv\,dt$ collisions—that is to say, in the time dt, $N\bar{z}\,dv\,dt$ molecules start new paths, leaving dv. As all directions are equally probable, the number which leave dv and move towards the small area $dxdy$ is the number of paths starting in dv during dt multiplied by the ratio of the surface cut out by the solid angle subtended at dv by $dxdy$, $dxdy \cos\theta$, to the surface of the sphere of radius r drawn about dv. Here r is the distance from dv to $dxdy$ and θ is the angle the line r makes with the z-axis. Of this number of molecules moving towards $dxdy$, only the fraction $e^{-\frac{r}{L}}$ goes the distance r or more without suffering a collision and being diverted. Thus the total number of molecules leaving dv during dt that pass through $dxdy$ is

$$N\bar{z}\frac{dxdy\cos\theta}{4\pi r^2}e^{-\frac{r}{L}}dvdt.$$

Now if, on the average, it is supposed that a molecule possesses the x component of velocity appropriate to the scene of its last collision, each of the above molecules carries an amount of momentum

$$m\left(u_o + r\cos\theta\frac{du}{dz}\right)$$

from dv through $dxdy$. Hence the momentum transfer is

$$-\frac{Nmu_o\bar{z}\,dxdy\,dt}{4\pi}\frac{\cos\theta}{r^2}e^{-\frac{r}{L}}\,dv - \frac{Nmr\cos^2\theta\frac{du}{dz}e^{-\frac{r}{L}\bar{z}}\,dxdy\,dv\,dt}{4\pi r^2}$$

The negative sign indicates that the momentum is being carried from greater to lower values of z. This quantity must be integrated for r from $r = 0$ to $r = \infty$. It must also be integrated so that dv covers all the space above the xy plane. To do this,

dv must be replaced by $dr(r \sin \theta d\phi)(rd\theta)$ and θ integrated from 0 to $\frac{\pi}{2}$, and ϕ from 0 to 2π. Thus the momentum transfer going through $dxdy$ downward from the space above the xy plane is given by the quantity

$$N_{dxdy\downarrow} = -\frac{Nm\,\bar{z}\,dxdy\,dt}{4\pi}\left[u_o\int_o^\infty e^{-\frac{r}{\bar{L}}}dr\int_o^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_o^{2\pi}d\phi + \frac{du}{dz}\int_o^\infty re^{-\frac{r}{\bar{L}}}dr\int_o^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_o^{2\pi}d\phi\right].$$

In a similar manner, the momentum transfer from below the xy plane upward from a volume $r^2\cos\theta d\theta d\phi dr$ in a time dt may be found as

$$N_{dxdy\uparrow} = \frac{Nm\,\bar{z}\,dxdy\,dt}{4\pi}\left[u_o\int_o^\infty e^{-\frac{r}{\bar{L}}}dr\int_o^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_o^{2\pi}d\phi - \frac{du}{dz}\int_o^\infty re^{-\frac{r}{\bar{L}}}dr\int_o^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_o^{2\pi}d\phi\right],$$

the $-$ sign inside the bracket being due to the fact that below the xy plane $u = \left(u_o - r\cos\theta\frac{du}{dz}\right)$. Adding the two terms $N_{dxdy\downarrow}$ and $N_{dxdy\uparrow}$ to get the net transfer M, it is found that the first members of the two expressions cancel and there is obtained on integration for the net transfer per unit area per second, *i.e.*, the viscous drag, the quantity

$$\frac{M}{dxdy\,dt} = -\frac{4\pi Nm\bar{z}L^2}{3(4\pi)}\frac{du}{dz} = -\frac{1}{3}Nm\bar{c}L\frac{du}{dz} = -\eta\frac{du}{dz},$$

since $$\bar{z} = \frac{\bar{c}}{L}.$$

Thus one has

$$\eta = \frac{1}{3}Nm\bar{c}L.$$

This was precisely what was found in the preceding section.

The integration here was carried out assuming $\bar{z}$ to be a constant. Its assumed value $\frac{\bar{c}}{L}$ was the value which one would have obtained using the Maxwell value for the mean collision frequency which is assumed independent of the velocity c as shown in Sec. 39. To take account of the variation, the Tait expression for the mean collision frequency must be used.

The treatment given by Tait, which is the more rigorous one, differs from the one given above only at the point where the integration of the free paths takes place. In this treatment, Maxwell's law of distribution is assumed to hold even though it applies strictly only to equilibrium. However, the quantity which before was written as $\bar{z} = \frac{\bar{c}}{L}$ is no longer so. L is a function of c. If the free path for a given c be taken as l and if one writes for N not a constant N, but N_c, giving the number of molecules with velocities between c and $c + dc$, the equation found above for M becomes

$$M = -\frac{2m\,dxdy}{4\pi}\frac{dt}{dz}\frac{du}{dz}\left[\int_o^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta \int_o^{2\pi} d\phi \int_o^{\infty} r\bar{z}e^{-\frac{r}{l}}dr \int_o^{\infty} \frac{4N}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}}dc\right].$$

The integral with respect to θ and ϕ leads to the factor $\frac{2\pi}{3}$. Again, in place of the collision frequency $\bar{z} = \frac{\bar{c}}{L}$, one now writes $z = \frac{c}{l}$, where l is a function of c, which is given by the Tait free-path equation (Sec. 39) as

$$l = \frac{\sqrt{2\pi}\frac{c^2}{\alpha^2}L}{\psi\left(\frac{c}{\alpha}\right)},$$

where L is the Maxwell free path. Thus the equation for $M = N_{dxdy\downarrow} + N_{dxdy\uparrow}$ becomes

$$M = -\frac{1}{3}Nm\,dxdy\,dt\frac{du}{dz}\left[\int_o^{\infty} l^2 e^{-\frac{r}{l}}r\frac{dr}{l^2}\int_o^{\infty}\frac{4}{\alpha^3\sqrt{\pi}}\left(\frac{c}{l}\right)c^2 e^{-\frac{c^2}{\alpha^2}}dc\right]$$

or, calling $\frac{c}{\alpha} = x$,

$$M = -\frac{1}{3}Nm\,dxdy\,dt\frac{du}{dz}\frac{4}{\sqrt{\pi}}\int_o^{\infty}\int_o^{\infty} lcx^2 e^{-x^2}e^{-\frac{r}{l}}\frac{rdr}{l^2}dx.$$

Integrating this for dr first, setting $c = x\alpha$ and $l = \frac{\sqrt{2\pi}x^2L}{\psi(x)}$, then

$$\frac{M}{dxdy\,dt} = -\eta\frac{du}{dz} = -\frac{1}{3}Nm\frac{du}{dz}\frac{\alpha L\sqrt{2\pi}}{\sqrt{\pi}}\int_o^{\infty}\frac{4x^5e^{-x^2}dx}{\psi(x)}.$$

This complicated integral was evaluated by Tait and led to the value

$$\int_0^\infty \frac{4x^5 e^{-x^2} dx}{\psi(x)} = 0.838.$$

Therefore

$$\eta = \frac{1}{3} Nm\alpha(0.838\sqrt{2}L)$$

or

$$\eta = \frac{1}{3} Nm\bar{c}L\left(0.838\sqrt{\frac{\pi}{2}}\right)$$

$$\eta = 1.051\left(\frac{1}{3} Nm\bar{c}L\right),$$

that is, the Tait value for the viscosity is 5.1 per cent higher than the value deduced by the Maxwell form of averaging. Physically, this difference is caused by the fact that the faster moving molecules have longer free paths and thus carry more momentum. This, if taken account of in averaging, as was here done, leads to the viscosity being greater because of the added effect of the longer free paths.

In his masterpiece, "The Dynamical Theory of Gases," Jeans[1] investigates what he calls the "persistence of velocity" after collision in the impact of elastic spheres. This analysis carried out for elastic spheres of equal mass and of velocities c and c' evaluates α, the *average component of velocity of one molecule c along its initial direction after impact*, for all values of the velocities c and c'. Dividing this average component by the initial velocity c the average "expectation" α/c of a velocity after collision is obtained. It is seen from the table below how α/c varies with the ratio of c/c'. The average persistence

c/c'	∞	4	2	1½	1	⅔	½	¼	0
α/c	0.500	0.492	0.473	0.441	0.400	0.368	0.354	0.339	0.333

$(\alpha/c)_e$ in a molecular collision under a Maxwellian distribution is 0.406. For elastic spheres of different mass one can write

$$\left(\frac{\alpha}{c}\right)_m = \frac{m_1 - m_2}{m_1 + m_2} + \frac{2m_2}{m_1 + m_2}\left(\frac{\alpha}{c}\right)_e,$$

where $(\alpha/c)_m$ is the expectation with a mass m_1 of velocity c colliding with a mass m_2 of velocity c', and $(\alpha/c)_e$ is the expectation for equal masses given before. A series of average values of $(\alpha/c)_m$ for different values of the ratio m_2/m_1 in a gas is given

below. It is clear that under these conditions c and c' are also functions of m_1 and m_2. Hence one can express $(\alpha/c)_e$ in terms of the values of the ratio m_2/m_1, corresponding to c'/c.

m_2/m_1	0	1/10	1/5	1/2	1	2	5	10	∞
$(\alpha/c)_m$	1.000	0.879	0.779	0.573	0.406	0.243	0.152	0.086	0.000
$(\alpha/c)_e$	0.333	0.335	0.339	0.360	0.406	0.432	0.491	0.498	0.500

This persistence of velocities must now be taken into account in the analysis of the coefficient of viscosity. Jeans considers the expression for the coefficient of viscosity including the Tait free path (page 212), which is here expressed as

$$\eta = \frac{1.051}{3} N m \bar{c} L_M$$

in order to see what effect the persistence of velocity has on it. Now on the average each molecule has experienced a path whose projection on the z-axis is ζ. In its previous path it had a velocity component along z of w, of which the expectation θ leads one to assume that it retains on the average a component of velocity θw along z. Hence the expectation of the projection of this path along z may be taken as $\theta\zeta$. Going back one collision farther, the expectation of its projection along z in the path of the projection ζ considered is given by $\theta(\theta\zeta) = \theta^2\zeta$. Thus going back to earlier and earlier paths, each one contributes a diminishing amount to the expectation of ζ. Thus the motion of the molecule due to past motions will have come with a velocity component along z not of w but of $w + \theta w + \theta^2 w + \theta^3 w + \ldots$, and hence the projection of its path on z will not be ζ but

$$\zeta + \theta\zeta + \theta^2\zeta + \ldots = \zeta/(1 - \theta).$$

Hence the molecule will not on the average have come with a momentum appropriate to the plane $z = z_0 \pm \zeta$ but from a point $z = z_0 + \zeta/(1 - \theta)$, where θ measures the average expectation of persistence. Now actually one cannot increase the amount of momentum transferred across the boundary by a projection like ζ in the proportion to the persistence of the path, for the intervening impacts have disturbed the transfer of a momentum in a succession of paths. Jeans assigns one-half of its excess momentum to each colliding molecule. Thus the effect on

the momentum transfer is that of the particle having come undisturbed from a region of last impact not $\zeta/(1 - \theta)$ away but a distance given by

$$\zeta + \frac{1}{2}\left\{\theta\zeta + \frac{1}{2}\left[\theta^2\zeta + \frac{1}{2}(\theta^3\zeta + \ . \ . \ . \ )\right]\right\} = \frac{\zeta}{1 - \frac{1}{2}\theta}.$$

As $\theta = 0.406$ for a uniform gas, this expression becomes 1.255ζ. This factor 1.255 Jeans then feels justified in multiplying into L_m in the viscosity equation, as it represents the *effective increase in the free path* as far as momentum transfer due to persistence goes. Hence, according to Jeans,

$$\eta = \frac{1.051}{3} N m\bar{c} L_M (1.255)$$
$$= \frac{1.317}{3} N m\bar{c} L_M.$$

A more accurate calculation in which the factor $1/(1 - \theta/2)$ is introduced into the integrand for the mean free path in the Tait calculation gives a factor 1.382 instead of 1.317. Hence Jeans, as a result of his persistence of velocities correction, writes

$$\eta = \frac{1.382}{3} N m\bar{c} L_M = 0.461 N m\bar{c} L_M.$$

Jeans, recognizing the approximate nature of his equation for persistence, points out that attempts at improving the equation from this point of view are useless in that the more powerful mathematical methods used by Chapman and by Enskog yield more justified and accurate values. As a result of Chapman's analysis the constant in the equation for η for elastic spheres turns out to be 0.499 instead of 0.461 as computed by Jeans. Thus one can accept as the best value of the expression for the coefficient of viscosity, on the assumption of elastic solid spherical atoms, the equation

$$\eta = 0.499 N m\bar{c} L_M.$$

60. Agreement between Elementary Theory and Observation for the Coefficient of Viscosity.—The expression deduced for η, $\eta = \frac{1}{3} N m\bar{c} L$, with some uncertainty in the value of the constant

⅓ depending on the method of averaging, can be transformed for discussion as follows. Since

$$L = \frac{1}{\sqrt{2}\pi\sigma^2 N},$$

it follows that

$$\eta = \frac{m\bar{c}}{3\sqrt{2}\pi\sigma^2}.$$

1. It is seen at once that, since $\bar{c} \propto \sqrt{1/m}$, η should vary as $\sqrt{m}$. For gases this holds quite accurately if account be taken of the variation of σ, which is comparatively small for most gases.

2. Furthermore, the expression is independent of pressure, for neither m, $\bar{c}$, nor σ is a function of pressure. This surprising relation was deduced before the value of η as a function of pressure had been measured. Investigation[3] showed it to be true for pressures from a few mm of mercury up to several atmospheres, contrary to expectation, for it seemed absurd that the viscous drag of a rarefied gas should be the same as for a dense one. At low pressures the relation fails, since the mean free path then becomes comparable to the dimensions of the apparatus and the assumptions used in deducing η no longer hold (see Sec. 77). At very high pressures, where attractive forces between the molecules become appreciable, the relation might again be expected to fail, for momentum transfer of the liquid type begins to occur (see Sec. 64).

3. Again, the $\bar{c}$ above can be replaced by $\sqrt{\frac{8R_AT}{\pi N_A m}}$, where N_A is the Avogadro number, m the mass of a molecule, R_A the gas constant, and T the absolute temperature. Thus $\eta = \frac{2}{3\pi^{3/2}\sigma^2}\sqrt{mkT}$, where $k = R_A/N_A$, the Boltzmann constant. This predicts that η should vary as the square root of the absolute temperature. Experiment[4] shows that η increases with temperature more rapidly than this and does not follow a simple power of T. The failure of this prediction to hold depends on the erroneous assumption that σ is independent of T. The value of σ depends on the mean distance of approach of the molecules on impact. This depends on the repulsive and attractive forces between molecules and their energy of agitation. Since increased T

means an increase in kinetic energy, and hence a lessened effect of attractive forces on the free paths of the molecules, as well as a closer approach on impact, it is not surprising that η is found to increase more rapidly with T than the $\sqrt{T}$. If η were found proportional to T, then σ would only have to vary as $1/\sqrt[4]{T}$ to cause this. This is not a very rapid change. It seems, however, worth while to point out that the deviation is not serious from the point of view of the establishment of the kinetic theory, for it predicts an increase in η with T which is nearly fulfilled, whereas previous experience with liquids showed the reverse effect. The deviation is, however, very welcome, as it makes it possible to test the variation of σ, the apparent diameter, with T and thus leads to an evaluation of intermolecular forces. This will be discussed more at length in Sec. 63, under the theory of Sutherland.

The measurements of η afford the best values of L obtainable. Thus a check of the theory from the point of view of a prediction of the value of η from theory and a comparison with the observed values is meaningless, for L otherwise determined is far less exact. It is interesting to compute η at 0°, 760, for N_2 from σ derived from Van der Waals' b and compare it with the observed value. For air, $\sigma = 3.53 \times 10^{-8}$ cm,

$$m = 28.0 \times 1.66 \times 10^{-24} \text{ gram } \bar{c} = 4.54 \times 10^4 \text{ cm/sec.}$$

$$\eta = \frac{28.0 \times 1.66 \times 10^{-24} \times 4.54 \times 10^4}{3\sqrt{2}\pi\ 1.245 \times 10^{-15}}.$$

$$\eta = 1.27 \times 10^{-4}.$$

The value of η observed for N_2 at 0° is

$$\eta = 1.66 \times 10^{-4}.$$

The values agree in order of magnitude but differ by about 23 per cent. Part of this discrepancy would be taken care of by the Tait free path. If a constant in the equation computed by Jeans,[1] including a correction for what he terms the persistence of velocities, were used, a very good agreement would result in this case. It is seen, therefore, that, while the result is approximately correct, the question of the constant factor is an important one. Again, it must be pointed out that it is questionable to *apply values of σ obtained from critical data to viscosity theory*, for the real significance of a value of σ depends on the measurements from which it is deduced. Thus it is quite probable that

the value of σ entering into b is not the same as the one used for viscosity.

61. Criticisms of the Simple Theories.—In what has preceded, certain points were passed over as sufficiently accurate, with little or no comment. Two of these merit further discussion and will be taken up in this section.

The first limitation of the development is that it postulates that the state of motion is nearly steady, *i.e.*, that the speed of the gas stream at any point does not vary much with the time. This requirement is introduced by the fact that no distinction is made between the time at which the molecules leave the volume element dv and the time at which they cross the surface element $dxdy$. The numerical magnitude of this limitation will be estimated later.

A second point bears on the validity of the assumption that *on the average, a molecule possesses the x-component of momentum appropriate to the scene of the last collision.* The analysis of this assumption and associated ones occurring in the theory of heat conduction and diffusion have been treated by Jeans[1] under the designation of *persistence of velocities.* The analysis pertaining to this correction is given in his "Dynamical Theory of Gases," and only the results will be given in this text.

Passing now to the more detailed study of the first of these corrections, it is important to determine *the thickness of the gas layer in which practically all of the viscous action takes place.* In the theory of Maxwell the momentum transfer is integrated over all space. Actually, however, the distant volume elements contribute practically nothing to the viscous action across $dxdy$. The expression for η after integration over the polar angles θ and ϕ is

$$\eta = \frac{1}{3} Nm \frac{\bar{c}}{L} \int_0^\infty e^{-\frac{r}{L}} r dr = \frac{1}{3} Nm\bar{c}L.$$

If one consider the viscous action of those molecules whose last collision occurred at a place less than d distant from the place of crossing $dxdy$, this will be less than the total amount by the following fraction of the total viscous action:

$$\int_d^\infty e^{-\frac{r}{L}} \frac{r dr}{L^2} = e^{-\frac{d}{L}} \left(\frac{d}{L} + 1 \right).$$

This shows that all but about 4 per cent of the viscous action across a surface is effected by the crossing of molecules within a distance of five times the mean free path from the place of crossing, while all but 0.3 per cent is gained by including molecules from distances up to eight times the free path. The conclusion is that virtually all of the viscous action in a gas occurs over an extremely thin layer of the gas.

The result of the preceding analysis makes it possible to form an estimate of the amount of the error made in neglecting the distinction between time of leaving dv and time of crossing $dxdy$. Molecules coming from a greater distance than $8L$ need not be considered and the time for the average molecule to go this distance is given by $8L/\bar{c}$, a quantity whose order of magnitude is 10^{-9} sec. Thus the deviations from the steady state occurring in practice are unimportant in their effect on the theory. This is especially true, since modern methods utilize only the steady state.

62. Viscosity and Intermolecular Forces. Repulsive Force Fields.—In Sec. 59 the expression for the coefficient of viscosity was deduced assuming molecules that were elastic spheres exerting no attractive forces on each other. In Sec. 60 it was intimated that the failure of the equation deduced in Sec. 59 in regard to the observed temperature variation of η was due to the fact that the molecules (1) exerted attractive forces on each other and (2) that the molecules were not rigid elastic spheres but centers of repulsive force which varied rapidly with the distance. It was in fact shown in Chap. V that molecules interacted approximately as configurations that had forces between them of the form $\phi(r) = \frac{D}{r^m} - \frac{G}{r^n}$, where m was of the order of 6, and n of the order of from 9 to 14. To date the problem of the effect of such a law of force on the value of η has not been very completely studied, due largely to the complicated nature of the problem. It is clear that if one regards the molecules not as elastic spheres but as centers of repulsive force of the form $f(r) = -\frac{G}{r^n}$, the distance of approach of molecular centers σ in impact must be a function of the energy of impact such that the apparent molecular diameter σ is a function of the temperature. Again it must be recognized that as molecules exert attractive forces on each other the collision

frequency must be greater than if no attractive forces existed. Furthermore such forces must also cause deviations from the straight-line free paths *without elastic solid impact* which result in energy and momentum exchanges affecting the coefficient of viscosity. Such actions are governed by the law $F(r) = +\frac{D}{r^m}$ and, as the energies and hence velocities increase with increasing temperature, the effect of such forces must decrease. Both the decrease in the value of σ for repulsive forces and the decrease in the alteration of free paths, with consequent reduction of collisions due to attractive forces, must in the end cause an apparent decrease in the molecular radii as temperature increases. Hence the mean free path and therefore also η must increase as temperature increases, aside from any change in η due to the quantity $\bar{c}$ in the simple expression for η. It is this apparent variation of σ and L with temperature that causes η to vary more rapidly than $\sqrt{T}$ which is predicted by simple theory. It must also be clear from the material given in Chap. V that the variations of σ, L, and therefore η, for different gases must be different as $\phi(r)$ is so widely different for different gases. Thus in H_2 and He it was seen that Chapman[27] was able to calculate the law of repulsive force in good agreement with data from the equation of state from the variation of η with temperature, although the law of attractive force was used in a convenient but inexact form, *i.e.*, $m = 3$. This lay in the fact that in these cases the attractive forces were negligible and the variation of σ could be accounted for almost entirely by the repulsive terms. The agreement in the case of more strongly attracting gases was, on the other hand, not so satisfactory. It is thus clear that until the *complete* law of attractive force as a whole can be used in the study, it is necessary to account for the variation in η with temperature on the basis either of attractive forces alone or of repulsive forces alone. Thus it happens that in most cases two approaches to the problem are possible for approximate studies of the phenomenon: some gases being best treated by a consideration of repulsive forces, others by a consideration of the attractive forces. It will accordingly be of interest to regard both of these approaches in order to gain a clearer insight into the problem.

Repulsive Forces.—Jeans,[29] in the third edition of his "Dynamical Theory of Gases," shows that in molecular impact the kinetic

energy of motion which has been consumed in overcoming the repulsive forces at σ, the closest distance of approach, is $\frac{1}{3}mC^2$ or kT. Hence the *mutual potential energy* of two molecules at a distance σ, corresponding to the repulsive force occurring at an impact at a temperature T, will be kT. The *force* of repulsion at the distance σ is therefore $-k\frac{dT}{d\sigma}$.

If the repulsive force is of the form Gr^{-n}, one can then write $Gr^{-n} = -k\frac{dT}{d\sigma}$ which on integration gives $\sigma_1 = \left[\frac{G}{kT(n-1)}\right]^{1/(n-1)}$ In such an encounter, the distance σ_1 is *not the same as the diameters of two equivalent spherical elastic molecules* colliding after straight paths in such a way as to give the same angular deflection. σ_1 will exceed this diameter by a factor depending on n and will only equal that of the solid molecules when one has elastic solid impacts $n = .\infty$. Ignoring this difference, it is seen that, in any case, σ will vary as $(1/T)^{1/(n-1)}$ so that $1/\sigma^2$ will vary as $T^{2/(n-1)}$, whence η will vary as T^s where $S = \frac{1}{2} + \frac{2}{n-1}$. It has in fact been found that for many substances η does vary as T^s.

In general, then, one can introduce this variation of σ into the equation for the coefficient of viscosity. It was found that for elastic-solid impacts

$$\eta = \frac{0.499Nm\bar{c}}{\sqrt{2}\pi N\sigma^2} = \frac{0.499m\sqrt{\frac{8}{\pi}\frac{kT}{m}}}{\sqrt{2}\pi\sigma^2} = \frac{A\sqrt{mkT}}{\sigma^2}.$$

Replacing σ by the expression above, one obtains

$$\eta = A\sqrt{mkT}\left[\frac{kT(n-1)}{G}\right]^{\frac{2}{n-1}},$$

where A is a numerical constant. Chapman has determined the value of the constant A to be

$$A = \frac{5\sqrt{\pi}}{8I_2(n)\Gamma\left[4 - \frac{2}{(n-1)}\right]}$$

to a first approximation where $I_2(n)$ is defined on page 221 of Jeans. With this value of A the equation reduces to Maxwell's[30]

exact equation, when $n = 5$ and to the equation $\eta = 0.491\frac{m\bar{c}}{\sqrt{2}\pi\sigma^2}$ when $n = .\infty$. A second approximation for $n = .\infty$ gave a correction factor of 1.01485 to A which agrees with a factor found by Enskog[31] for this same case of 1.01485. Thus it is seen that this approach gives an expression for η fairly closely in agreement with facts and giving absolute values of η which are in agreement with most of the more exact studies.

63. Viscosity and Intermolecular Forces: Attractive Force Fields. Attractive Forces.—The first one to take account of the attractive forces in studying the effect of η on the coefficient of viscosity was Sutherland.[5] He considered two elastic solid spherical molecules of radii σ_0, attracting each other with a force $F(r)$ which varies as the distance r in some fashion unspecified. To study the effect of such attractions on each other, one must consider the two molecules moving toward each other with a relative velocity C. The otherwise straight-line paths under the attractive forces will be transformed into orbits about a common center of gravity whose character must depend on the masses, velocities, and initial directions of motion. Since the problem involves only the interaction of two molecules independent of any frame of reference, it is clear that the orbits will lie in a plane. Since the motion is purely relative, one can in this case assume one molecule as fixed and consider the other as moving with a velocity whose magnitude and direction are identical with the relative velocity. These simplifications enable one at once to apply the laws of orbits under central forces to the problem.[6,28]

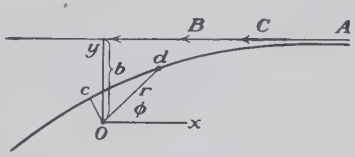

FIG. 39.

Consider the fixed molecule at O of Fig. 39 and the moving molecule to have started at infinity along a path AB, with a velocity C, which is the relative velocity. Owing to the forces, the molecule will describe an orbit Adc about O, an instantaneous position of the molecule being designated as d where Od is the radius vector r, and the angle ϕ measured from Ox parallel to AB is the angular displacement of the molecule at d. Let Oy of length b be the perpendicular on the initial path and Oc be the apsidal distance, or distance of closest approach. Ox and Oy are along the x- and y-axes of a rectangular coordinate

system about O. To simplify calculations let the molecule be one of unit mass. The equations of motion then are[6,28]

$$\frac{d^2x}{dt^2} = -F(r)\frac{x}{r}, \qquad \frac{d^2y}{dt^2} = -F(r)\frac{y}{r}.$$

Multiply the equations respectively by y and x and subtract, then

$$y\frac{d^2x}{dt^2} - x\frac{d^2y}{dt^2} = 0, \text{ or } \frac{d}{dt}\left(y\frac{dx}{dt} - x\frac{dy}{dt}\right) = 0.$$

Now

$$x = r\cos\phi,\ dx = -r\sin\phi d\phi.$$
$$y = r\sin\phi,\ dy = r\cos\phi d\phi.$$

Whence

$$y\frac{dx}{dt} - x\frac{dy}{dt} = -r^2\frac{d\phi}{dt}.$$

Hence

$$\frac{d}{dt}\left(r^2\frac{d\phi}{dt}\right) = 0 \text{ and } r^2\frac{d\phi}{dt} = h, \text{ or } \frac{d\phi}{dt} = \frac{h}{r^2}.$$

Here h is a constant of integration which is twice the areal velocity of the molecule.

On multiplying the first and second initial equations of motion by dx/dt and dy/dt, respectively, and adding them, one obtains

$$\frac{dx}{dt}\left(\frac{d^2x}{dt^2}\right) + \frac{dy}{dt}\left(\frac{d^2y}{dt^2}\right) = -F(r)\left(\frac{x}{r}\frac{dx}{dt} + \frac{y}{r}\frac{dy}{dt}\right)$$

or

$$\frac{1}{2}\frac{d}{dt}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2\right] = -\frac{F(r)}{r}\frac{1}{2}\frac{d}{dt}(x^2 + y^2).$$

But $(dx/dt)^2 + (dy/dt)^2 = C^2$, the square of the velocity of the moving molecule, and $x^2 + y^2 = r^2$, whence

$$\frac{d(C^2)}{dt} = -\frac{F(r)}{r}\frac{d(r^2)}{dt} = -2F(r)\frac{dr}{dt}.$$

One can call θ the supplement to ϕ, *i.e.*, $\theta = 180 - \phi$, and describe the vector velocity c at d in terms of its polar components along r and perpendicular thereto by $c^2 = (dr/dt)^2 + (rd\theta/dt)^2 = (dr/dt)^2 + h^2/r^2$, whence

$$\frac{d(c^2)}{dt} = \frac{2dr}{dt}\frac{d^2r}{dt^2} - \frac{2h^2}{r^3}\frac{dr}{dt} = -2F(r)\frac{dr}{dt},$$

so that

$$\frac{d^2r}{dt^2} - \frac{h^2}{r^3} = -F(r).$$

Now h, the areal velocity, is constant, for, if multiplied by the mass of the particle, this gives the moment of momentum which is conserved. At $r = \infty$ the velocity is C, and the lever arm of the velocity is the perpendicular b. Hence $h = Cb$. Thus $d^2r/dt^2 = b^2C^2/r^3 - F(r)$. One can then integrate from $r = r$ to $r = \infty$, for, at $r = \infty$, $(dr/dt) = C$, the velocity lying entirely along the asymptote. Thus one obtains

$$C^2 - \left(\frac{dr}{dt}\right)^2 = \frac{b^2C^2}{r^2} - 2\int_r^\infty F(r)dr.$$

At the apse of the orbit, *i.e.*, at the closest point of approach, the radius vector r_0 is perpendicular to the orbit and $dr/dt = 0$. For this point

$$0 = C^2 - \frac{b^2C^2}{r_0^2} + 2\int_{r_0}^\infty F(r)dr,$$

which gives

$$b^2 = r_0^2\left[1 + \frac{2}{C^2}\int_{r_0}^\infty F(r)dr\right].$$

This equation relates the perpendicular distance b of the fixed molecule on the initial orbit of the moving molecule, and r_0 the distance of closest approach to the velocity and the law of attractive force. It is seen that actually $\int_{r_0}^\infty F(r)dr$ is the relative potential energy at $r = r_0$, while $C^2/2$ is the relative kinetic energy, KE, at infinite separation. Hence $b = r_0$ if the potential energy, PE, is 0, *i.e.*, for forceless molecules, and b^2 is greater than r_0^2 in the measure that $1 + (PE/KE)$ is greater than 1. Now it is the curvature of the paths that result in collisions which could not take place in the absence of forces. Thus, if σ_0, the separation of the moving and fixed molecules at elastic impact, is greater than r_0 or equal to it, then as a result of the forces the molecule projected with the velocity C on a path whose perpendicular from O is b, or less, will be sure to collide with the molecule at O. In other words, if σ_0 is the diameter of the solid elastic spherical molecules, an impact which would only occur if $b \gtrless \sigma_0$ will as a result of attractive forces occur when b is less than or equal to b_0, given by

$$b_0^2 = r_0^2\left\{1 + \frac{2}{C^2}\int_{r_0}^{\infty} F(r)dr\right\} = \sigma_0^2\left\{1 + \frac{2}{C^2}\int_{\sigma_0}^{\infty} F(r)dr\right\}.$$

Thus the *apparent molecular diameter* b_0 *is greater than the real diameter* σ_0. It is seen that as $\int_{\sigma_0}^{\infty} F(r)dr$ decreases, b_0 approaches σ_0 and for forceless elastic spheres the two are equal. It is seen, however, that the value of σ_0 is not influenced by the temperature as is really the case for interactions of repulsive force fields.

As a consequence of this deduction it is seen that in mean-free-path equations and in equations involving mean free paths for molecules with attractive forces the σ^2 must be replaced by b_0^2. Hence, for molecules exerting attractive forces the mean free path of the Maxwell form becomes

$$L_m = \frac{1}{\sqrt{2}\pi N\sigma_0^2\left\{1 + \frac{2}{C^2}\int_{\sigma_0}^{\infty} F(r)dr\right\}}.$$

Now the quantity $\frac{2}{C^2}\int_{\sigma_0}^{\infty} F(r)dr$ is a constant except for C^2 which is proportional to the absolute temperature T. Hence one can write

$$\frac{2}{C^2}\int_{\sigma_0}^{\infty} F(r)dr = \frac{K}{T},$$

where K is a constant depending on $F(r) = D/r^m$ and σ_0. Thus

$$L_m = \frac{1}{\sqrt{2}N\pi\sigma_0^2\left(1 + \frac{K}{T}\right)}.$$

Accordingly

$$\eta = 0.499Nm\bar{c}L_m = \frac{0.499\rho\bar{c}}{\sqrt{2}\pi N\sigma_0^2\left(1 + \frac{K}{T}\right)}.$$

Thus η is proportional to

$$\frac{\sqrt{T}}{1 + \frac{K}{T}}, \qquad \text{or} \qquad \eta_T = \eta_0\sqrt{\frac{T}{T_0}}\,\frac{1 + \frac{K}{T_0}}{1 + \frac{K}{T}},$$

where η_T is the coefficient at T, and η_0 is the coefficient at T_0. This expression, first derived by Sutherland,[5] gives excellent

numerical agreement for many gases. In the case of CO_2, $K = 277$; and this value gives agreement to 2 parts in 1,000 from 18 to 224°C.

A closely similar equation results from the studies of Reinganum.[7] As was shown in Sec. 50, Reinganum took into account the fact that the molecules attract each other in such a way that the number of molecules per unit volume at a distance r from a molecule attracting others according to a force $F(r)dr$ is given by $N = N_0 e^{-\int_r^\infty F(r)dr/kT}$, where N_0 is the concentration to be expected in the absence of forces. The increase in density of the molecules given above applies to a distance r from the molecule in question which extends from σ_0 to ∞. This density increase varies from some value at σ_0 to 0 at ∞ at a rate which depends on $F(r)dr$. To consider the effect of this increased density on the *mean* free path and viscosity, one must replace the N in the mean-free-path equation, which influences the frequency of collision, by $N_0 e^{-\left[\int_r^\infty F(r)dr\right]/kT}$, in which the $\int_r^\infty$ is carried out so as to extend from $\bar{r}$ some mean value of r to ∞, where $\bar{r}$ lies between σ_0 and ∞. Thus N becomes $N = N_0 e^{-\int_{\bar{r}}^\infty F(r)dr/kT} = N_0 e^{K/T}$, where K is again a constant depending on $F(r) = Dr^{-m}$, $\bar{r}$, and T. The value of the exponent is positive as $-\frac{1}{k}\int_{\bar{r}}^\infty Dr^{-m}dr = +K$, a constant.

Hence Reinganum's consideration leads to the expressions:

$$L_m = \frac{1}{\sqrt{2}\pi N_0 e^{\frac{K}{T}} \sigma_0^2} \quad \text{and} \quad \eta = \frac{0.499\rho\bar{c}}{\sqrt{2}\pi N_0 \sigma_0^2 e^{\frac{K}{T}}}.$$

This equation, it is to be observed, makes η vary as $\sqrt{T}e^{-K/T}$. In practice it fits as well as Sutherland's equation for many gases, and for esters and Hg vapor it is satisfactory over an even greater range. This is not strange for Sutherland's equation is really just a first-order approximation to this one. For small values of T one can write $e^{K/T} = 1 + \frac{K}{T} + \frac{K}{T^2 2!} + \ldots$, so that, neglecting higher powers of T than the first, it agrees with Sutherland.

Actually neither equation is completely satisfactory for two reasons. Both assume elastic solid molecules such that the apparent diameter σ_0 is not a function of temperature due to the variation of the distance of approach on impact which repulsive forces of the usual type demand. In the second place neither takes into account momentum and direction exchanges due to close approach without actual impact between the molecules at a distance σ_0. On any attractive theory there are such transfers of momentum, and an accurate calculation must include these. The inclusion of such exchanges may, however, not vitally change the results as the agreement observed with experiment suggests. An estimate of the effect of this second item can be had in the case of the attraction between *ions* and *molecules* where an inverse-fifth-power law obtains.[32] In this case calculated on an elastic-solid-impact theory by J. J. Thomson, the result indicates that the non-impact exchanges produce an apparent increase of the diameter of about 10 per cent beyond that produced by the elastic solid impacts.

64. Viscosity and Intermolecular Forces: Simultaneous Attractive and Repulsive Force Fields.—In 1929 Hassé and Cook[33] published a paper in which they extended the analysis of the equation of viscosity to the case where a law of force of the form $\phi(r) = Dr^{-m} - Gr^{-n}$ obtains. The analysis was carried out in a general way for this case without specifying m and n. For comparison of experiment and theory a definite set of values for m and n must be chosen so that the complicated integrals involved may be numerically evaluated. Hassé and Cook chose the values of m and n as 5 and 9, respectively.

For the general case they obtained

$$\eta = \frac{5}{8}\left(\frac{\pi M}{2h}\right)^{\frac{1}{2}} \frac{(hG)^{-\frac{2}{n-1}}}{D_1},$$

where $h = \frac{1}{2}RT$, R being the gas constant, and

$$D_1 = \Gamma\left[4 - \frac{2}{(n-1)}\right] I_2(n, m; 0) + A\left(\frac{2D}{M}\right)\left(\frac{hM}{2}\right)^{\frac{n-m}{n-1}} \left(\frac{2G}{M}\right)^{\frac{1-m}{n-1}} \Gamma\left(3 - \frac{3-m}{n-1}\right)$$

The quantity I_2 is an integral involving n, m, and k, where k is a quantity derived from t corresponding to the apse of the relative

orbit. A is a numerical constant which depends on the values of m and n. This equation gives a variation of η with temperature of the form

$$\eta = \frac{BT^{\frac{1/2+2}{(n-1)}}}{\left(1 + ST^{\frac{m-n}{n-1}}\right)},$$

where $B = \dfrac{5(\pi M)^{1/2}R^{\frac{1/2+2}{(n-1)}}}{2^{\left(3-\frac{2}{(n-1)}\right)}G^{\frac{2}{n-1}}\Gamma\left(4 - \frac{2}{n-1}\right)I_2(n, m; 0)}$, and S is a generalized Sutherland constant. For $n = \infty$, the equation develops into the ordinary Sutherland equation. For $m = 3$, one obtains

$$\eta \propto \frac{T^{3/2}}{T^{\frac{n-3}{n-1}} + S_1}$$

which is the Lennard-Jones equation referred to in Chap. V which was used to determine n for various gases to be used in comparison with n computed from the equation of state. S_1 is the S of the equation above for the special value of m used.

The calculation of the value of η for $m = 5$, $n = 9$, yields the result

$$\eta = \frac{5}{32}\left(\frac{MRT}{\pi}\right)^{1/2}\left(\frac{D}{G}\right)^{1/2}\frac{S^{1/2}}{I(S)}.$$

Here $S = (2RTG)^{1/2}/D$, and $I(S)$ is an integral for which a table of values in terms of numerical values of S depending on the force constants D and G has been computed. This equation for viscosity, it is seen, has in it only the two unknown coefficients of the force law, D and G, which must be computed for each gas for which $m = 5$, $n = 9$ is applicable.

On the basis of this equation, values of D and G for a number of gases are computed for these gases by a graphical method from the experimental values of η and T. The data permit of an evaluation of the "diameter" defined by Lennard-Jones as

$$\sigma_n = \left[\frac{2Gn}{3(n-1)R}\right]^{\frac{1}{n-1}}$$

which for the values of the index 9 or 5 gives $\sigma = (G/12R)^{1/6}$ and $\sigma' = (D/6R)^{1/4}$. The gases tested were Ar, H_2, N_2, Air, CO_2, Hg, and Ne. The best values of D and G are given in the table

below, together with values from the equation of state. The latter are indicated by parentheses.

Gas	D	G
Argon	3.23×10^{-43} (1.62×10^{-43})	1.09×10^{-72} (1.01×10^{-72})
H_2	3.54×10^{-44} (2.54×10^{-44})	1.06×10^{-73} (0.92×10^{-73})
N_2	3.11×10^{-43} (1.82×10^{-43})	1.54×10^{-72} (1.58×10^{-72})
Air	3.05×10^{-43}	1.45×10^{-72}
CO_2	8.5×10^{-43}	5.8×10^{-72}
Hg	5.05×10^{-43}	8.95×10^{-74}
Neon	Gives no fit, n should be 13	

The table below gives the values of η in hydrogen for the temperatures listed in column 1. Column 2 gives the observed values of $\eta \times 10^7$. In column 3 the values computed from Hassé and Cook's equation are given, with the force constants deduced by them. In column 4 the values from the same equation using the constants from the equation of state are listed; and in column

Viscosity of Hydrogen

T (abs.)	$\eta 10^7$ (obs.)	$\eta 10^7$ (a)	$\eta 10^7$ (b)	$\eta 10^7$ (c)
457.3	1,212	1,226	1,253	1,207
373.6	1,046	1,060	1,082	1,052
287.6	877	878	896	875
273.0	844	846	863	843
261.2	821	820	836	816
255.3	802	806	822	803
233.2	760	756	770	757
212.9	710	708	722	709
194.4	670	664	676	666
170.2	609.3	603	614	608
89.63	392.2	380	388	389
70.87	319.3	320	328	329
20.04	105–111	111	125	137

5 the values calculated by Kammerlingh-Onnes on the basis of a law of force varying as $r^{-11.2}$ are found.

The curve of Fig. 40 is plotted between the values of log $S^{1/2}/I(S)$ and log S. The points experimentally observed are indicated. There are two essentially linear portions connected by a curve. The linear portions correspond to regions where the attractive and repulsive forces largely determine η, the former being active at high temperatures where log S is about 0.2, and the latter at low temperatures where log S is about 1.4. In between, both factors are of importance. These curves

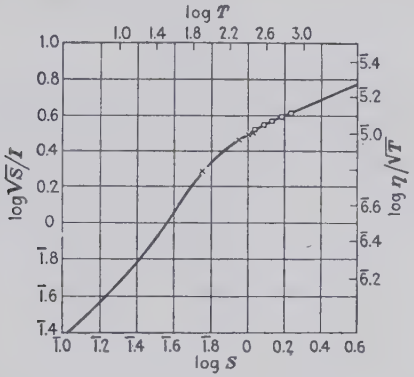

FIG. 40.

are drawn for $m = 5$ and $n = 9$. Experimental deviations from these curves at low values of T would indicate the proper value of n to choose for a gas. Then, having chosen an n, the deviations would indicate what alteration in m is needed. For high values of T one could first infer the value of m and then later adjust for the correct value of n. As is seen, the experimental values of η for air which cover the widest range do not enable one to decide on n or m in this fashion. This is in fact the greatest drawback to a proper evaluation of these important constants. In the range of temperatures studied, the values chosen appear to be relatively satisfactory.

A study of the discrepancies between the values of D and G deduced from the viscosity equation and those obtained from the equation of state, together with an analysis of the values of σ and σ' calculated for $n = 9$ and $n = \infty$ as well as other considerations, seem to indicate that the equation for η is satisfactory and that the discrepancies involved are to be ascribed largely to the value of $m = 5$ chosen for the attractive force

for all the gases. It is to be expected that m should vary from gas to gas.

It is seen from this study that the theory as developed on the assumption of a force law of the form $\phi(r) = Dr^{-m} - Gr^{-n}$ is relatively satisfactory. So far the accuracy given by this very involved and lengthy calculation is such that further real and easy progress must require a much more accurate and extended range in the experimental study of η at various temperatures.

65. Measurement of Viscosity.—Before closing this topic, in view of materials to be discussed in Chap. VII, it is desirable to discuss briefly the methods of measuring viscosity. The oldest method is based on the study of the rate of flow of the fluid through a capillary tube. The flow of liquids through capillaries was first studied systematically by Jean Louis Marie Poisseuille,[8] a French anatomist, who was interested in the physics of the circulation of the blood. His work was published in 1842. Other methods are based on the measurement of the damping of the oscillations of pendula,[9] the constant deflecting force of a cylinder in a rotating gas,[10] the fall of small spheres through a gas,[11] etc.

The foundation of all the methods lies in the solution of the hydrodynamical problem of fluid motion corresponding to the arrangement used. The theory of some of the methods is simple, while others lead to difficult problems in partial differential equations. The student who is interested in the hydrodynamic side of viscous fluid flow is referred to Lamb's[12] "Hydrodynamics."

In deriving Poisseuille's empirical formula from hydrodynamics it is assumed that all motion of the fluid is parallel to the length of the tube. This requires that the tube be very long compared with its diameter in order that irregular end effects be negligible. At the wall of the tube the fluid slips, so that the difference in speed between the wall and the fluid adjacent to it is

$$v = \frac{\eta}{\epsilon}\frac{\partial u}{\partial z},$$

in which ϵ is the "coefficient of external friction" (see Chap. VII, Sec. 77). The solution of the appropriate differential equations then yields for the volume of fluid flowing through the tube in unit time (Sec. 77)

$$V = \frac{\pi P}{8\eta L}\left(R^4 + \frac{4\eta}{\epsilon}R^3\right),$$

in which P is the pressure difference between the two ends, L is the length of the tube, and R is its radius. If there is no slipping of the gas along the walls, $\epsilon = \infty$ and the formula is

$$V = \frac{\pi P R^4}{8\eta L}.$$

Graetz[13] gives the corresponding solutions for capillaries of other forms than circular cross section. Osborne Reynolds[14] has shown that above the critical velocity

$$v = \frac{2{,}000\eta}{2R\rho},$$

in which ρ is the density of the fluid, the motion becomes turbulent, and Poisseuille's law fails. Most of the research work on gas viscosity has been carried out by the study of the flow of gas in capillary tubes.

A method, capable of high precision, which has probably given the best recent results, is that of the constant deflection of a cylinder in a rotating mass of gas. This is described by Gilchrist[15] and by E. R. Harrington.[16]

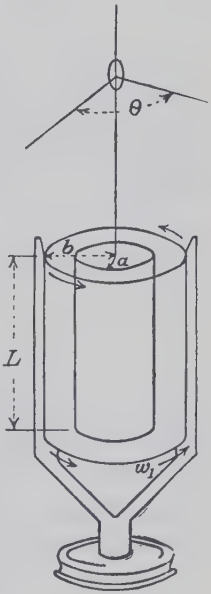

FIG. 41.—Rotating cylinder method for measuring viscosity of gases.

In this method a cylinder (Fig. 41) is hung up by a delicate suspension so that it may turn about a vertical axis. Surrounding the cylinder is a larger one which is rotated at a uniform speed. The gas is set in motion and the viscous forces which act on the inner cylinder cause it to turn until these forces are balanced by the torsional action of the twisted suspension. Let it be supposed that the radius of the inner cylinder is a and that of the outer cylinder is b, while the angular velocity of the outer cylinder is w_1. Let L be the length of the cylinders. In the steady state the speed of the gas will be zero at the inner cylinder and bw_1 at the outer cylinder. The force on an imaginary cylinder of radius r in the gas will be

$$F = 2\pi r L \eta \frac{\partial v}{\partial r}$$

and the moment of this force is

$$\overline{Fr} = 2\pi r^2 L\eta \frac{\partial v}{\partial r}.$$

By $\partial v/\partial r$ is to be understood the rate of change of the relative motion of adjacent layers of the liquid. To find this one may write

$$v = rw,$$

then

$$\frac{\partial v}{\partial r} = w + r\frac{\partial w}{\partial r}.$$

However, the w on the right-hand side arises from the variation in v which would be present if the gas rotated with uniform angular velocity, like a rigid body, when certainly no viscous action is developed. This term therefore does not enter into the value of $\partial v/\partial r$ to be used in the analysis. As a measure of the rate of shear of the gas one then has $\frac{\partial v}{\partial r} = r\frac{\partial w}{\partial r}$, and hence

$$\overline{Fr} = 2\pi r^3 \eta L \frac{\partial w}{\partial r}$$

gives the torque which each outer gas layer exerts on the adjacent one inside. In the steady state the torque exerted by each layer must balance the reaction of that which each adjacent layer exerts, since the angular acceleration of the gas is zero, that is, $\overline{Fr}$ is constant throughout the gas. The preceding equation may be now integrated as follows:

$$\overline{Fr}\int_a^b \frac{dr}{r^3} = 2\pi\eta L\int_0^{w_1} dw$$

$$\overline{Fr}\left[\frac{1}{a^2} - \frac{1}{b^2}\right] = 4\pi\eta L w_1$$

or

$$\overline{Fr} = 4\pi\eta L\frac{a^2b^2}{b^2 - a^2}w_1.$$

The torque $\overline{Fr}$ is that exerted on the inner cylinder. It is measured by the angle of deflection of the inner cylinder, the amount of torque for a given angle of deflection being first determined by independent experiments, that is to say, $\overline{Fr} = T_0\theta$, where T_0, the torsional constant of the fiber, may be found from the period of oscillation of the cylinder.

References

1. Jeans, J. H.: "Dynamical Theory of Gases," Chap. VIII, Sec. 352, p. 260; Chap. IX, Sec. 371, p. 275, Cambridge University Press, Cambridge, 1921. (Dover Reprint)
2. Maxwell, J. C.: *Phil. Mag.*, **19,** 20, 1860.
3. Maxwell, J. C.: *Phil. Trans. Roy. Soc.*, p. 249, 1886. Meyer, O. E.: *Pogg. Ann.*, **125,** 40, 564, 1865; **143,** 14, 1871; *Wied. Ann.*, **32,** 642, 1887. Crookes, W.: *Phil. Trans. Roy. Soc.*, p. 387, 1881. Warburg and Babo, *Wied. Ann.*, **148,** 203, 1873. Kundt and Warburg, *Phil. Mag.*, **50,** 53, 1875; *Pogg. Ann.*, **155,** 337, 525, 1875.
4. Meyer, O. E.: *Pogg. Ann.*, **148,** 203, 1873. Meyer and Springmuhl: *Pogg. Ann.*, **148,** 526, 1873. Fisher, W. J.: *Phys. Rev.*, **24,** 385, 1907; **28,** 73, 1909. See Fisher for a review of literature.
5. Sutherland, W.: *Phil. Mag.*, **36,** 507, 1893.
6. Moulton, F. R.: "Introduction to Celestial Mechanics," Chap. IV, The Macmillan Company, 1914. Webster, A. G.: "Dynamics of Particles," G. R. Teubner, Leipzig, 1912. Routh, E. J.: "Dynamics of a Particle," Cambridge University Press, Cambridge, 1898.
7. Reinganum: *Phys. Z.*, **2,** 242, 1900.
8. Poisseuille, J. L. M.: *Societé Philomath.*, p. 77, 1838; *Compt. Rend.*, **11,** 961, 1041, 1840; **12,** 112, 1841; **15,** 1161, 1892.
9. Tomlinson, H.: *Phil. Trans. Roy. Soc.*, **177,** part II, p. 767, 1886. Maxwell, J. C.: *Phil. Trans. Roy. Soc.*, p. 249, 1886.
10. Gilchrist, L.: *Phys. Rev.*, **1,** 124, 1916.
11. Rankine, A. O.: *Proc. Roy. Soc.*, **A84,** 181, 1911.
12. Lamb, H.: "Hydrodynamics," Chap. XI, Cambridge University Press, Cambridge, 1895. (Dover Reprint)
13. Graetz: *Schtömlich's Z. Math.*, **25,** 316, 1879.
14. Reynolds, Osborne: *Phil. Trans. Roy. Soc.*, **174,** 935, 1883; and **177,** 171, 1886.
15. Gilchrist, L.: *Phys. Rev.*, **1,** 124, 1913.
16. Harrington: *Phys. Rev.*, **8,** 738, 1916.
17. Warburg and Babo: *Wied. Ann.*, **17,** 390, 1882.
18. Phillips, P.: *Proc. Roy. Soc.*, **A87,** 48, 1912.
19. Bestelmeyer: *Ann. Physik*, **13,** 944, 1904.
20. Markowski: *Ann. Physik*, **14,** 742, 1904.
21. Schmidt: *Ann. Physik*, **30,** 393, 1909.
22. Zimmer, O.: *Verh. d. Deut. Phys. Ges.*, **14,** 471, 1912.
23. Onnes, K.: *Proc. Amst. Acad.*, **15,** 1386, 1913.
24. Rankine, A. O.: *Proc. Roy. Soc.*, **A83,** 265, 1910.
25. Smith, C. J.: *Proc. Roy. Soc.*, **34,** 155, 1922.
26. Rankine, A. O., and Smith: *Proc. Roy. Soc.*, **34,** 181, 1922.
27. Chapman: Under the title of "The Kinetic Theory of a Gas Composed of Spherically Symmetrical Molecules," Chapman discussed this question in a series of papers: *Phil. Trans. Roy. Soc.*, **A211,** 433, 1912; **A216,** 279, 1915; **A217,** 115, 1916; *Proc. Roy. Soc.*, **A93,** 19, 1916; *Phil. Mag.*, **48,** 593, 1924.
28. Jaeger, G.: "Fortschritte der Kinetischen Gastheorie," Chap. V, pp. 92 ff., Vieweg und Sohn, Braunschweig, 1919.

29. Jeans, J. H.: "Dynamical Theory of Gases," Chap. XI, p. 281.
30. Maxwell, J. C.: "Collected Works," Vol. II, p. 1. Jeans, J. H.: *Loc. cit.*, Chap. IX, p. 230.
31. Enskog: "Kinetische Theorie der Vorgänge in Mässig Verdünnten Gasen," Inaugural Dissertation, Upsala, 1917.
32. Loeb, L. B.: "Kinetic Theory of Gases," 1st ed., Sec. 108, p. 460.
33. Hassé and Cook: *Proc. Roy. Soc.*, **A125**, 196, 1929.
34. Lennard-Jones: *Proc. Roy. Soc.*, **A106**, 463, 1924; **A107**, 157, 1925; **A112**, 214, 1926.

II. HEAT CONDUCTION

66. Definition of Heat Conduction.—In Sec. 56 the transfer of heat in a gas by the molecules of the medium was shown to occur in two ways. The first mechanism depends on the effect of the earth's gravitational field on the changes in density produced by the temperature gradients, and was termed "convection." It is the result of mass motion of the gas, and consequently is not directly a kinetic phenomenon. A treatment of such mode of transfer falls primarily into the domain of hydrodynamics. The second mode of transfer operates in all cases of gaseous heat conduction and it constitutes an essential phase of the exchange of heat between the layers of different temperatures set up by convection. As was stated, it depends on the direct transfer of kinetic energy by molecules of one layer with a higher energy to molecules of lower average energy in another layer. Thus it is a strictly molecular phenomenon and may be treated by the kinetic theory.

As the gravitational field of the earth is ever present, it becomes very difficult practically to avoid the occurrence of convection in the experimental study of conduction. By the proper choice of orientation of the plates in the gravitational field (*e.g.*, placing them normal to the earth's field, the hotter one above), by use of low gas pressures, and by the use of very narrow gaseous gaps the convection may be relegated to a relatively insignificant place in the heat transfer between the surfaces considered.

If two large horizontal planes are assumed, the upper one at a temperature T_1, the lower one at a temperature T_0 separated a distance d, the quantity of heat Q transferred from one plate to the other through a gas across an area A in a time t is given by

$$Q = KA(T_1 - T_0)f(d)t,$$

where $f(d)$ stands for some function of d. As the distance d is decreased, the equation takes on the form

$$Q = KA\frac{T_1 - T_0}{d}t.$$

This is precisely the relation found for the case of unidirectional flow of heat through a large plane of solid substance by conduction. The occurrence of this equation indicates that all convection has ceased and that one may consider K, the constant of proportionality, to have the same meaning as that given for solids. Experiment shows that it is a constant for each kind of gas. Thus when convection is eliminated in a gas, heat transfer follows the same laws as for solids, the gas having a constant for heat conductivity characteristic of itself. The constant depends on the speed with which molecules of a higher energy content can diffuse into regions of lower energy content through the gas, that is, it is really a function of the rate of molecular transfer of kinetic energy from layer to layer. In solids the conduction of heat[3] seems to be an entirely different phenomenon, although the mechanism is little understood. In these bodies the molecules are rigidly bound in equilibrium positions by elastic forces. Their heat motions are then oscillations about their positions of equilibrium. To what extent heat conductivity depends on the transfer of energy from one quasi-elastically bound molecule to its nearest neighbor is little known. The close ratio of electrical conductivity of metals to their heat conductivity, evidenced by the Wiedemann-Franz[1] law, has suggested a more kinetic picture of this conduction. It seems possible that there exist, in the metals at least, free electrons in some numbers, darting here and there through the regular channels between the evenly spaced molecules. Such electrons were supposed to lead to the thermionic emission[2] and the electrical conductivity. On the basis of the Wiedemann-Franz law, it may be possible that they are also instrumental in the heat conductivity. If this were so, the mechanism in some solids could be considered similar in nature to gaseous conduction. On the whole, it is probably safer to assume that the elastic vibrations play the predominating rôle. Thus, although gaseous conduction obeys the same law as conduction in solids, it probably is due to an entirely different mechanism. It is not surprising, therefore, that the K for gases increases as T increases, while the similar quantity for metals decreases.

It is more accurate to write $\frac{T_1 - T_0}{d}$ in the differential form denoting d as dz, an element of distance chosen along the z-axis normal to the plates. It must be remembered, in representing $\frac{T_1 - T_0}{d}$ by $\frac{dT}{dz}$, that the flow always takes place from the hotter to the colder point.* The magnitudes of heat conductivity K for various types of conductors are given below to familiarize the reader with the magnitudes involved. K in the c.g.s. system gives the calories carried across 1 cm^2 in a second when there is a temperature gradient of 1°C. per cm normal to the plates.

TYPICAL VALUES OF K

Gas or substance	Temperature, degrees centigrade	K
Air	0	0.0000568
He	0	0.000339
H_2O (liquid)	0	0.00143
Paper	..	0.0003
Brick	..	0.0015
Al	18	0.504
Cu	13	1.00
Ag	18	1.00

67. The Simple Kinetic Theory of Heat Conduction.—The considerations involved in the evaluation of K are quite analogous to those involved in the evaluation of η as given in Sec. 58. With K, however, it is not momentum that is transferred, but kinetic energy. With this difference the two simple deductions are essentially parallel.

Assume the gas arranged in layers normal to the z-axis, the warmer layers being uppermost. Then T depends on z only. When the steady state is reached, as much heat flows out of any layer at a given time as flows into it, that is, from the equation of continuity[4] for this case, $d^2T/dz^2 = 0$, and integration leads to an equation which states that (dT/dz) is a constant. Hence at

* This is usually indicated by writing $Q = -KA\frac{dT}{dz}$, the minus sign indicating a negative slope to the T–z curve. At this point the minus sign is immaterial.

any point of the gas $T = T_0 + \frac{dT}{dz}z$, where dT/dz is positive in the arrangement under consideration. One-third of all the molecules are moving along the z-axis, or one-third of all the velocity components lie along z. These are the molecules which carry heat from one layer to the other. If the mean free path be L, one may, as before, consider a layer of thickness L. The average temperature difference of the molecules on the two sides of this layer will then be $L\frac{dT}{dz}$. If each molecule has a mass m and the specific heat of the gas is C_v,* the difference in energy content of the molecules is $mC_vL\frac{dT}{dz}$. Of the third of the molecules moving along z, one-half are moving downward. In 1 sec. $\frac{1}{6}N\bar{c}$ molecules pass downward through each cm² of the layer L and carry energy which is equal to $\frac{1}{6}N\bar{c}mC_vL\frac{dT}{dz}$ downward. Here N is the number of molecules per cm³ and $\bar{c}$ is the average velocity. Likewise, $\frac{1}{6}N\bar{c}$ molecules pass upward and they carry $-\frac{1}{6}N\bar{c}mC_vL\frac{dT}{dz}$ in energy units upwards across 1 cm² in unit time. The negative sign comes in here, as the gradient below the T_0 plane is negative. The total energy transfer is the difference of the energy carried down and that carried up. Taking this difference, one has Q/At, the energy carried per cm² per second, as

$$\frac{Q}{At} = \frac{1}{3}N\bar{c}mC_vL\frac{dT}{dz}.$$

But by definition $\frac{Q}{At} = K\frac{dT}{dz}$.

Hence $$K = \frac{1}{3}Nm\bar{c}LC_v.$$

Since, however, $\eta = \frac{1}{3}Nm\bar{c}L$, one has the interesting relation,

$$K = \eta C_v.$$

This equation is also the one obtained from the more complete derivation which takes into account the distribution of velocities

* This would be strictly true for a monatomic gas where there is only energy of translation in C_v. It seems that where rotational energy is concerned the contribution to this in C_v might be expected to be involved in the energy transfer to its full value. This does not seem to be true, as will be seen in Sec. 69.

as well as the distribution of free paths. Neither of these deductions is strictly rigorous and a discussion of the values of K will follow at the end of Sec. 69, where a more rigorous treatment is outlined. The elementary reader would do well to read the introduction to Sec. 69 and, omitting the mathematics, read the discussion at the end of the section. In the next section the more complete deduction, taking into account the distribution of free paths and velocities, will be given.

68. Deduction of the Constant of Heat Conduction, Taking into Account the Distribution of Free Paths and Velocities.—To derive the expression for the transfer of energy from one layer of

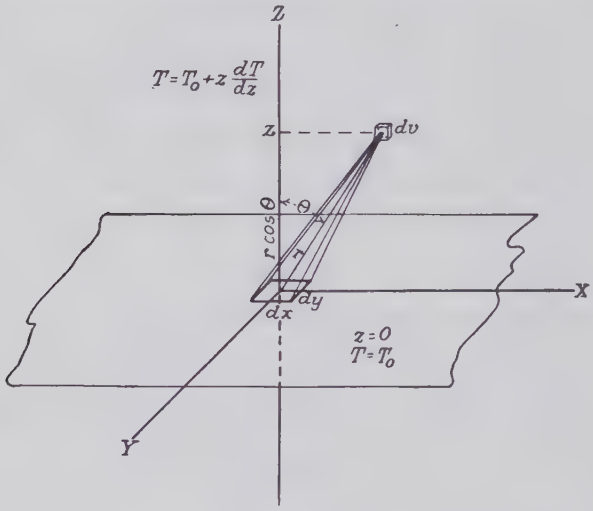

FIG. 42.

the gas to the other by the molecules, one may proceed as follows: Assume a gas space large in extent having a uniform temperature gradient, the temperature above being higher than that below. Assume that the steady state has been reached and consider the transfer of heat across the xy plane taken normal to the temperature gradient along the z-axis. At the xy plane assume the temperature to be T_0. Thus above xy the temperatures will be $T = T_0 + z\frac{dT}{dz}$ and below this plane the temperatures will be $T = T_0 - z\frac{dT}{dz}$. To start with, attention may be concentrated upon a small area $dxdy$ of the xy plane (Fig. 42) and the total

number of molecules crossing this in unit time from above and below considered. The net energy transfer due to these molecules will give the total heat conduction and hence determine K. Consider a small volume dv at r cm from $dxdy$ such that the line r connecting dv and $dxdy$ makes an angle θ with the normal to $dxdy$, *i.e.*, with the z-axis. Thus z for the volume dv is $r \cos \theta$. If each of the molecules in dv has a mean free path L and a velocity c, then each molecule starts a *new free path* c/L times a second. Now in dv there are $Ndv\frac{4}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc$ molecules having a velocity between c and $c + dc$, where N is the number of molecules in a cm^3. Hence $\frac{4N}{\alpha^3\sqrt{\pi}}\frac{c}{L}dvc^2e^{-\frac{c^2}{\alpha^2}}dc$ molecules of speed c will leave dv in a second (see Sec. 35). Of these, the number in a cone of base $dxdy \cos \theta$ will have paths directed towards θ if all directions are equally probable. That is, $\frac{dxdy \cos \theta}{4\pi r^2}\frac{4}{\alpha^3}\frac{N}{\sqrt{\pi}}\frac{c^3}{L}dve^{-\frac{c^2}{\alpha^2}}dc$ particles will leave dv per second headed for $dxdy$ along r. Of these, the fraction $e^{-\frac{r}{L}}$ (see Sec. 21) only will succeed in crossing $dxdy$ without impact. As each of these is assumed to have an energy corresponding to the position of dv in the region in which heat is being transferred, its temperature will be

$$T_z = T_0 + z\frac{dT}{dz}.$$

Each molecule that leaves dv will then carry an amount of energy

$$mC_v\left(T_0 + z\frac{dT}{dz}\right)$$

from dv through $dxdy$, where m is the mass of a molecule and C_v is the specific heat. Thus the energy carried from dv in a time dt through $dxdy$ by the molecules of all speeds is

$$dE = \frac{-Ndxdy \cos \theta dvdtmC_v}{4\pi r^2 L}e^{-\frac{r}{L}}\left(T_0 + r\cos\theta\frac{dT}{dz}\right)\frac{4}{\alpha^3\sqrt{\pi}}\int_0^\infty c^3e^{-\frac{c^2}{\alpha^2}}dc$$

$$= -NdxdydtdvmC_v\frac{\bar{c}}{L}\left[\frac{T_0e^{-\frac{r}{L}}\cos\theta}{4\pi r^2} + \frac{\cos^2\theta\frac{dT}{dz}e^{-\frac{r}{L}}}{4\pi r}\right]$$

where the evaluation of $\int_0^\infty \frac{4}{\alpha^3\sqrt{\pi}} c^3 e^{-\frac{c^2}{\alpha^2}} dc$ gives the quantity $\bar{c}$. Since $dv = (rd\theta)\ (r \sin \theta d\phi)\ dr$, the total energy transferred from the whole hemisphere is the integral of dr from 0 to ∞, of $d\theta$ from 0 to $\pi/2$, and of $d\phi$ from 0 to 2π. Hence the amount of energy transferred from above the xy plane downward in the time dt is $\frac{dQ}{dt}\downarrow$.

$$\frac{dQ}{dt}\downarrow = \frac{-N\bar{c}dxdymC_v}{L}\left[\frac{T_0}{4\pi}\int_0^\infty e^{-\frac{r}{L}}dr\int_0^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_0^{2\pi}d\phi\right.$$
$$\left. + \frac{1}{4\pi}\frac{dT}{dz}\int_0^\infty re^{-\frac{r}{L}}dr\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi\right].$$

In a similar fashion the energy transferred from below the xy plane upward amounts to

$$\frac{dQ}{dt}\uparrow = \frac{+Ndxdy\ \bar{c}mC_v}{L}\left[\frac{T_0}{4\pi}\int_0^\infty e^{-\frac{r}{L}}dr\int_0^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_0^{2\pi}d\phi\right.$$
$$\left. - \frac{1}{4\pi}\frac{dT}{dz}\int_0^\infty re^{-\frac{r}{L}}dr\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi\right].$$

The $-$ sign in the $\frac{dQ}{dt}\downarrow$ indicates that the heat goes from a higher to a lower temperature, and the $-$ sign in the brackets in $\frac{dQ}{dt}\uparrow$ comes from the fact that below the xy plane the temperature at any point r cm away from $dxdy$ is $T_0 - r\cos\theta\frac{dT}{dz}$. Adding the two terms and integrating, the net energy transfer is

$$\frac{dQ}{dt} = -\frac{1}{3}Nm\bar{c}LC_v dxdy\frac{dT}{dz}.$$

But K is defined as

$$\frac{dQ}{dt} = -Kdxdy\frac{dT}{dz}.$$

Hence $K = \frac{1}{3}Nm\bar{c}LC_v = \eta C_v$, as was found before.

69. Correction of the Derivation of the Coefficient of Heat Conductivity and Comparison with Experiment.—The preceding

derivation, strictly speaking, was not rigorous, although it is experimentally valid in order of magnitude. The error lies in two effects. In the first place, since the pressure is constant (*i.e.*, since there is no mass motion in the gas), while T varies from place to place, the density of the gas must be variable and decreases as T increases. This means that N varies with z in such a fashion that $N = N_0 - z\frac{dN}{dz}$ above the xy plane and $N = N_0 + z\frac{dN}{dz}$ below this plane. In the second place, c varies with T and hence the collision frequency Ξ and the free path which depends on it c/Ξ are both functions of z. These were neglected in the previous derivation. This requires the use of the velocity free path and collision number in place of the terms c/L and L in the equations above. Finally, it was assumed that the Maxwell distribution law held in this derivation. Since this law is an equilibrium law, it cannot hold here, for heat conduction is *not an equilibrium phenomenon* (see Sec. 56). This error should not be neglected as it is of the same order of magnitude as the phenomenon itself. The neglect of this error in the cause of simplicity and for the purpose of a simple mechanical analysis of the problem is responsible for the serious discrepancies between theory and observation. It might be added in passing that the simple equation deduced above seems to fit as well as it does in view of these omissions since conduction takes place over short distances, so that the changes in N with r are comparatively small, and thus the errors introduced are not overwhelming.

The question of these corrections has been attacked from the point of view of this text by many workers. O. E. Meyer[5] and Jeans[6] have given the treatments which most closely reproduce the true state of affairs and are generally accepted. The treatment of Jeans follows the plan laid out by Meyer, adding, however, some corrections. Chapman[7] and Enskog,[8] using a different line of reasoning, have carried out a more accurate study applicable to monatomic gases and depending on the law of force assumed between the molecules. These treatments are, in the main, beyond the scope of this book, and for complete details the reader is referred to the original articles. It seems, however, instructive to note the way in which Meyer[5] introduces the corrections into this equation and to point out wherein Jeans extends them. This will be done briefly in what follows.

Let each molecule leaving the volume dv considered above carry with it the energy $\frac{1}{2}mc^2$ appropriate to the average molecular energy in dv. In this volume the mean collision frequency must now be represented by the factor Ξ in place of c/L and the mean free path under these conditions will be represented by c/Ξ. An analysis similar to that of Sec. 68 then leads to the expression for the energy transferred per second through $dxdy$ from a volume dv above the xy plane as expressed by

$$\frac{dQ}{dt} = \frac{mc^2}{2}\frac{dxdy\cos\theta}{4\pi r^2} r^2 \sin\theta d\theta d\phi dr \Xi e^{-\frac{\Xi r}{c}} \frac{4N}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc.$$

At this point in the analysis it is convenient to replace the α of the distribution law by the factor $1/\sqrt{hm}$ to conform to the equations used by Meyer and Jeans in order to facilitate comparison with these writers. This transformation is carried out in another portion of the text (Sec. 43). For convenience, it will be repeated in a footnote.* Collecting the terms and making the substitution, the total heat transfer from one side of the xy plane to the other through $dxdy$, after carrying out the proper integrations, may be represented as

$$\frac{dQ}{dt} = \frac{1}{2}m\int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} dxdy \sin\theta\cos\theta d\theta \int_0^{\infty} N\left(\frac{hm}{\pi}\right)^{3/2} dr \int_0^{\infty} c^4 \Xi e^{-\Xi\frac{r}{c}} e^{-hmc^2} dc.$$

The integrations to be performed are complicated by the added facts that $N = N_0 \mp \frac{dN}{dz} r\cos\theta$, and that $h = h_0 \mp \frac{dh}{dz} r\cos\theta$, the plus and minus signs referring to the regions above and below the xy plane, where $N = N_0$ and $h = h_0$. Since r is a small quantity, terms involving higher powers may be neglected and a substitution of these values for N and h makes the equation for the total energy transfer through $dxdy$ take the following form:

$$\frac{dQ}{dt} = \frac{1}{2}N_0 m\left(\frac{hm}{\pi}\right)^{3/2} \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} dxdy \sin\theta\cos\theta d\theta \int_0^{\infty} dr \int_0^{\infty} \Psi dc.$$

* $\frac{1}{3}NmC^2 = RT$. Calling $R/N = k$ the Boltzmann constant, one has $C^2 = 3kT/m$. As $\alpha^2 = \frac{2}{3}C^2$ (Sec. 35), one may write $\alpha^2 = 2kT/m$. If $h = 1/(2kT)$, α becomes $1/\sqrt{hm}$.

In this equation Ψ has the value given by

$$\Psi = c^4 \Xi e^{-\frac{\Xi r}{c}} e^{-hmc^2}\left[1 \pm \left\{\frac{1}{N_0}\frac{dN}{dz} + \left(\frac{3}{2h_0} - mc^2\right)\frac{dh}{dz}\right\} r \cos\theta\right].$$

The two quantities N and h vary simultaneously, thus for simplification of the integrations it may be best to express one in terms of the other. This is accomplished by means of certain conditions defining the equilibrium in the gas. They are included in the three following statements:

1. The mass of gas passing across the xy plane in any given time in both directions along the z-axis must be equal. If it were not, the density of the gas would vary as a function of the time, which it obviously does not, by definition of the pure conduction phenomenon.

2. There is no mass motion of the gas, hence the excess of momentum transfer parallel to the z-axis must be constant for every unit of cross section of the xy plane.

3. Since the conditions for heat transfer assumed that the net quantity carried along the z-axis is the same throughout the area studied, the same criterion of equal net heat transfer for any unit area of cross section of the xy plane must also hold.

These relations may be expressed in the form of equations, each of which contains an integral of the same form as the one considered above. The three integrals differ only in that in the first one, applying to condition 1, the factor $\frac{1}{2}mc^2$ is absent, that in the second, applying to condition 2, the $\frac{1}{2}mc^2$ is replaced by $mc \cos\theta$; while the third, applying to condition 3, is the original equation under consideration above.

In the integrals introduced by conditions 2 and 3 it may be assumed that N and h are linear functions of z. The first derivatives of these are then constant, and where they are multiplied by r (in itself small) they may be neglected for the present treatment.

The first integral, depending on the transfer of heat by a net mass movement of the gas, may be solved only through a consideration of the relation between N, Ξ, and h. Such a relation is obtained through simple integrations in the form of

$$0 = \int_0^\infty \frac{c^4}{\Xi} e^{-hmc^2}\left\{\frac{1}{N_0}\frac{dN}{dz} + \left(\frac{3}{2h_0} - mc^2\right)\frac{dh}{dz}\right\} dc.$$

Originally, O. E. Meyer integrated this equation making two approximate assumptions representing extreme conditions.

Taking a mean value of these two results, he arrived at a relation between N and h from this process that says that $\frac{1}{N_0}\frac{dN}{dz} = \frac{3}{4}\frac{1}{h_0}\frac{dh}{dz}$. W. Conrau actually integrated the correct expression by mechanical quadratures and found, instead of $\frac{3}{4}$ as the numerical factor, a factor 0.71066. Thus $\frac{1}{N_0}\frac{dN}{dz} = 0.71066\,\frac{1}{h_0}\frac{dh^*}{dz}$. Substituting this for $\frac{1}{N_0}\frac{dN}{dz}$, one at once has Ψ in a simplified form.

$$\Psi = c^4 \Xi e^{-\frac{\Xi r}{c}} e^{-hmc^2}\left\{1 - \left(\frac{2.21066}{h_0} - mc^2\right)\frac{dh}{dz}\, r\cos\theta\right\}.$$

Integration of Q, as far as is directly possible, for values of z above the xy plane and below it lead, on addition, to the net heat transfer per unit time as

$$\frac{dQ}{dt} = -Kdxdy\frac{dT}{dz} = -\frac{2\pi}{3}N_0 m\frac{dh}{dz}\left(\frac{hm}{\pi}\right)^{3/2}\int_0^\infty \frac{c^6}{\Xi}\left(\frac{2.2107}{h_0} - mc^2\right)e^{-hmc^2}dc.$$

It is then necessary to reduce hm and $m\frac{dh}{dz}$ to terms containing the temperature T and C_v, the specific heat at constant volume. Conversion of the units to heat units and comparison with the experimental equation of heat conduction $-K\frac{dT}{dz}dxdy$ leads to the evaluation of K in the following form:

$$K = \frac{8}{9\sqrt{\pi}}N_0 C_v h^{7/2} m^{7/2}\int_0^\infty \frac{c^6}{\Xi}\left(mc^2 - \frac{2.2107}{h_0}\right)e^{-hmc^2}dc.$$

* Equilibrium of mass distribution throughout the gas is one of the conditions of equilibrium on which the distribution law is founded. In assuming N a $f(z)$, an assumption was introduced contrary to this law. It led to the relation above

$$\frac{1}{N_0}\frac{dN}{dz} = 0.71066\,\frac{1}{h_0}\frac{dh}{dz}.$$

Had equality of density obtained, this expression would have been

$$\frac{1}{N_0}\frac{dN}{dz} = \frac{1}{h_0}\frac{dh}{dz}.$$

This discrepancy, Jeans points out, is the order of magnitude of the error introduced by the assumption of the distribution law holding accurately.

Again, in earlier papers Meyer integrated this by a method of approximation. At a later date, however, P. Neugebauer carried out the accurate integration and found that the value of the integral was such that K is given by

$$K = 0.5205\ N_0 m\bar{c} L C_v.$$

Since

$$\eta = \frac{1}{3} N_0 m\bar{c} L,$$

$$K = 1.56 \eta C_v.$$

If Meyer's value of η be used where $\eta_m = \frac{1}{\pi} N_0 m\bar{c} L$

$$K = 1.63\ C_v \eta_m$$

where η_m is Meyer's value of η.

Thus it is seen that a rigorous deduction brings a numerical factor into the relation $K/\eta C_v$ which is greater than unity. This factor is generally designated as ϵ and one may most properly write that

$$K = \epsilon \eta C_v$$

where ϵ varies from 1 to 2.57, depending on the mathematical analysis. The value of ϵ from theory, then, is not definite and depends on the extent to which approximations were made in deduction and how it was deduced.

This clearly indicates that the classical approach to the problem leaves much to be desired. In fact, it appears that, with a few minor improvements made by Jeans, the limit of accuracy of the classical method of Meyer has been reached. The reason for this lies in the assumption made that Maxwell's law holds throughout the gas while it is perfectly clear that in the absence of equilibrium it cannot hold. A consequence of this failure is pointed out in the footnote on page 244. Since the equations deduced yield the law $K = \epsilon \eta C_v$, and the improvements in the law merely alter ϵ, it is clear that the effect of persistence of velocities on the value of K will make itself felt in the value of η, as neither ϵ nor C_v is much affected by persistence.

The problem of the theory of heat conduction in gases can, however, be attacked by more general and powerful methods of analysis which do not start with the assumption of a particular distribution of velocities. While such methods do not depict the physical mechanisms at work, they permit of a far closer approximation to the exact solution. The methods were

initially developed by Boltzmann[15] and Maxwell[10] and were carried to their logical conclusion by Chapman[7] and by Enskog.[8] Their development requires a great deal more space than is available within the scope of this book. For information as to the methods used, the reader is referred to the introductory treatment given in Chaps. VIII and IX of Jeans'[16] "Dynamical Theory of Gases" and thereafter to the original papers of Chapman and Enskog which in themselves virtually amount to small monographs. In his approach, Chapman, on the basis of such broad assumptions as that the molecules have only energy of translation and that they have spherical symmetry, is able to lay down the conditions for mass, momentum, and energy transfer in gases and to solve the problem successfully once the laws of force for the atoms have been designated. Some force laws lead to expressions which are easily capable of solution such as repulsive forces of the inverse-fifth-power type which Maxwell[10] had already developed in his first study. Chapman's approach enables one (with much labor in some cases) to obtain the approximate solution of the problem for elastic spheres, any repulsive law of the form $1/r^n$, and a combination of attractive and repulsive forces of the inverse-power type.

Chapman in 1912 applied his generalized method and obtained for molecules with translational energy only, and spherical symmetry, the value

$$K = 2.5\eta C_v,$$

in which the coefficient ϵ has the value 2.5. This expression is so general that it applies *closely for all repulsive-force laws of the form* Gr^{-n}, which in Maxwell's case of $n = 5$ gives exactly $\epsilon = 2.500$. In a later paper Chapman found that further approximations alter the value of ϵ by less than 1 per cent. For the case of elastic spheres, $n = \infty$, he found $\epsilon = 2.522$. Enskog obtained an elaborate expression for ϵ for any value of n given by

$$\epsilon = \frac{5}{2} \frac{1 + \dfrac{(n-5)^2}{4(n-1)(11n-13)} + \cdots}{1 + \dfrac{3(n-5)^2}{2(n-1)(101n-113)} + \cdots},$$

which reduces to 2.5 when $n = 5$. The expression $\epsilon = 2.5$ is thus fairly accurate and satisfactory for all monatomic gases, although the repulsive force with $n = 5$, for which it holds

exactly, is not justified by experiment and leads to an incorrect variation of η with T. Thus the approximate value 2.5 of ϵ for monatomic gases depends on the bases of classical kinetic theory and is most insensitive to the particular law of force used.

On the other hand, the *simple* classical theory of heat conduction previously developed yields the value $\epsilon = 1$. The cause for this difference between the results of the two theories was pointed out by Eucken[17] in an admirable paper in 1913. It lies in the fact that, for *translatory motions only*, the molecules with greater values of velocity have longer free paths, so that they travel farther and carry more energy than do molecules of lower velocities. Hence the transport by molecules of the higher velocities is more effective and leads with the distribution of velocities to a greater total energy transfer than for molecules of *average* energy. Thus ϵ must actually have a value greater than the value $\epsilon = 1$ for the derivation of which the *averaged* velocities were used.

The consideration of this fact furthermore aids in the evaluation of ϵ for molecules having rotational and vibrational energy on a rational and semi-empirical basis which is in fairly good agreement with experiment, as Eucken shows. In this consideration one can start with the factor $\epsilon = 2.5$, which is the theoretically justified factor for translatory energy only and is derived from a theory which includes the considerations above. The Maxwell distribution law allows one to assume that the rotational energy of a molecule is completely independent of its translational energy so that a molecule with high rotational energy is just as likely to have a given translatory energy as a molecule with small rotational energy. Since rotational energy is not related to the translatory energy in a given molecule, the effect in translation which makes $\epsilon > 1$ does not apply to rotation, and ϵ_r, the value of ϵ for rotation, is unity. If C_t and C_r represent the contributions of translation and rotation to the specific heat at constant volume C_v (see Sec. 91), $C_v = C_t + C_r$. Then it is clear that K, where translation and rotation both occur, is given by

$$K = (\epsilon_t C_t + \epsilon_r C_r)\eta,$$

where $\epsilon_t = 2.5$ is the value of ϵ for translation, and $\epsilon_r = 1$ is that for rotation. Thus

$$K = \left(2.5\frac{C_t}{C_v} + \frac{C_r}{C_v}\right)C_v\eta = \epsilon\eta C_v.$$

For a monatomic gas, $C_r/C_v = 0$. For a diatomic gas with no vibration, $C_t/C_v = 3/5$ and $C_r/C_v = 2/5$ (see Sec. 91). Hence $K = [2.5(3/5) + 2/5]C_v\eta = 1.9C_v\eta$, whence, for a rigid diatomic molecular gas, $\epsilon = 1.9$, a value in general accord with the experiments, which in some cases lead to a slightly higher value. It is not known whether such deviation is due to experimental error or represents a real error in theory. For rigid triatomic molecules the value is $\epsilon = 1.75$.

For vibrational degrees of freedom the case is somewhat different. Vibrations along the direction of heat transport are in general associated with the energy of translation, as such energies arise from an impact in the direction of transfer. Accordingly one may assign to such a component of vibration the value $\epsilon > 1$ and set $\epsilon \sim 2.5$. If the vibration is normal to the direction of motion, its contribution is independent of the translational velocity in the direction of transport, and thus, as in rotation, $\epsilon = 1$. Therefore in the case of vibration, two vibrational components give $\epsilon = 1$, and one can be assumed to have $\epsilon = 2.5$. Hence ϵ for vibration takes on the average value of $\epsilon_s = \dfrac{2.5 + 1 + 1}{3} = 1.5$. This applies to molecules of a more complex nature when the vibrations are toward, and away from, the center of gravity, as the vibrations can always be resolved along three axes. It will thus apply to the more compact molecules but may fail in the case of the long chainlike organic molecules. For such molecules ϵ_s must approach 1. It must also be pointed out that since the value of ϵ was deduced on classical grounds, it must be expected to fail where (as frequently occurs for vibration) classical laws are replaced by quantum laws. Jeans,[18] for the sake of simplicity, goes on the assumption that ϵ_s is 1 in all cases as for rotation. On this assumption of Jeans, one can simplify the expressions given above and one obtains

$$\epsilon = \left(2.5\frac{C_t}{C_v} + \frac{C_r + C_s}{C_v}\right)$$
$$= \left(2.5 + \frac{C_r + C_s}{C_t}\right)\frac{C_t}{C_v}.$$

Calling $\frac{C_r + C_s}{C_t} = \beta$, one has at once

$$\epsilon = \frac{2.5 + \beta}{1 + \beta}.$$

Now, in Sec. 91,

$$\frac{C_p}{C_v} = \gamma = \frac{5 + C_r + C_s}{3 + C_r + C_s}.$$

with $C_t = 3$ in terms of this notation, where C_p is the specific heat at constant pressure. Hence

$$C_r + C_s = \frac{3\gamma - 5}{(1 - \gamma)}$$

and

$$\frac{C_r + C_s}{C_t} = \beta = \frac{3\gamma - 5}{3(1 - \gamma)},$$

whence

$$\epsilon = \frac{9\gamma - 5}{4}.$$

The values of ϵ derived from these equations may be compared with the observed values of ϵ in the table below. The gases used are given in column 1. In column 2 the observed values of ϵ are given while column 3 gives Eucken's value of ϵ and column 4 gives the value deduced on Jeans' equation given above. As is to be expected, both equations are nearly equally good. With the doubt as to the effect of ϵ_s there is more flexibility in Eucken's equation than in that of Jeans, so that the former equation can approximate the correct value more nearly than can Jeans'. On the other hand, while Eucken's equation depends on the theoretical values of C_t, C_r, and C_s, Jeans' equation uses the experimental values of γ. Doubtless some of the differences can be ascribed to experimental uncertainty, for the values of K, are not very accurately known, K being difficult to measure with precision. Again it must be remembered that the values for ϵ observed experimentally depend not only on the values of η and K, which can be in error by 1 per cent, but that C_v is also to be included in the calculation. C_v is, however, still less accurately known and is temperature dependent, as is notably the case for H_2 at low temperatures.

Eucken gives a detailed discussion of the deviations for different gases and suggests the sources of the discrepancies

obtained. In the case of He, especially at low temperatures, ϵ_t is less than 2.5, which probably indicates an imperfection in the energy-exchange mechanism. In H_2S, H_2O, NH_3, and CO the computed values for ϵ on Eucken's theory are greater than are the observed values. This may mean that ϵ_s is not zero or is greater than as assumed, or that energy exchanges on impact are not complete. For H_2 at low temperatures, the values observed clearly indicate the loss of rotational energy and the resulting decrease of C_v theoretically expected and experimentally observed (see Sec. 92). In N_2, O_2, and CO_2, but not in CH_4, there is an indication that MC_v must decrease by 5 to 10 per cent at low temperatures.

Gas	ϵ (obs.)	ϵ (calc.) Eucken	ϵ (calc.) Jeans
He	2.40	2.50	2.44
Ar	2.49		2.44
H_2	1.965	1.93	1.90
N_2	1.905	1.90	1.91
O_2	1.913		1.90
CO	1.835		1.91
NO	1.870		1.88
Cl_2	1.803	1.84	
SO_2	1.601	1.677–1.726	
CO_2	1.628	1.57 $\epsilon_s = 0$	1.72
N_2O	1.640	1.645–1.715	1.73
CS_2	1.59	1.436–1.581	
H_2S	1.435	1.73–1.745	
H_2O	1.25	1.70 $\epsilon_s = 0$	
C_2H_2	1.58	1.58–1.695	
NH_3	1.429	1.57 $\epsilon_s = 0$	
CH_4	1.715	1.69–1.73	
C_2H_4	1.53	1.54–1.66	1.55
C_2H_6	1.51	1.44–1.65	

It is therefore to be concluded that the more powerful methods of Boltzmann, Maxwell, Chapman, and Enskog are capable of solving the problem of the theoretical value of K for gases in a relatively satisfactory manner. The improvement to be expected lies in the more accurate approximation for various gases, once the force laws characteristic of them are definitely known, and in the more precise knowledge of the rotational and vibrational

energies and their individual effects on the transport of energy. Thus, except for a few individual gases, one can write $K = \epsilon\eta C_v$, where to 1 or 2 per cent $\epsilon = \frac{1}{4}(9\gamma - 5)$.

As regards the variation of K with pressure, and temperature, the same may be said as for viscosity, except that the variations of C_v with these factors must be taken into account. Thus K, the coefficient of heat conductivity, should be independent of pressure to the extent that C_v is independent of pressure. This was first enunciated by Maxwell.[11] It was confirmed experimentally first by Stefan[12] and later by others. This surprising law was found to hold from pressures at which convection ceased down to quite low pressures which are of the order of 1 mm of mercury. At still lower pressures K becomes less. But this action is due to the fact that below these pressures the mean free path becomes comparable to the dimensions of the vessel and the mechanism of heat transfer must be analyzed from a different standpoint (see Sec. 80). Again, assuming C_v constant, K should, as is the case for η, be theoretically proportional to the square root of the absolute temperature. It was found, however, that, owing to the decrease in the action of intermolecular forces with increasing temperature (*i.e.*, the apparent decrease of the diameter of the molecules from this cause), the mean free paths, and hence the coefficient of viscosity, increased more rapidly than with the square root of the absolute temperature. Thus K should vary in the same manner with temperature as η does, that is, K should increase with T faster than proportional to $\sqrt{T}$. Some preliminary experiments by Winkelmann[13] seemed to indicate this to be true. Measurements of K are, on the whole, very difficult and inaccurate in gases because of the difficulty in eliminating convection and radiation. Later experiments above 0°C. seemed to indicate that K increased less rapidly with T than the value of η. In fact, some experiments indicated that K was more nearly proportional to $\sqrt{T}$. *The results of the many experiments are none the less quite discordant, and little can be concluded from them.* Below 0°C. a much more rapid decrease in K with a decrease in T was noted, as was observed to be the case for viscosity and as is predicted by the theory of Sutherland[14] for viscosity. The conclusion to be drawn is that, in general, K shows the same trend with temperature that η exhibits, although the variation may not be accurately parallel.

On the whole, however, the success of the kinetic theory in predicting and evaluating the heat conduction has been striking, and the unexpected agreement of the predicted constancy of K with pressure variation was, indeed, a dramatic triumph. Needless to say, the inaccuracy of the measurements of K and the large uncertainty in ϵ make this coefficient of little use in determining L, the mean free path.

References

1. Wiedemann-Franz law: Winkelmann's "Handbuch der Physik," vol. 3, p. 471 ff., Johann Ambrosius Barth, Leipzig, 1906.
2. Secs. 41, 43, Chap. IV of this text.
3. Riecke, E.: Marx's "Handbuch der Radiologie," vol. 6, Chap. III, p. 319, Akademische Verlagsgesellschaft, Leipzig, 1925. Jeans, J. H.: "Dynamical Theory of Gases," Chap. XII, p. 302 ff., Cambridge University Press, Cambridge, 1921. (Dover Reprint)
4. Ingersoll and Zobel: Chap. II, p. 9, Ginn and Company, Boston, 1913.
5. Meyer, O. E.: "Kinetic Theory of Gases," Mathematical Appendix Nos. 55, 56, 57, p. 461 ff. English edition translated by Baynes; Longmans, Green & Co., London, 1899.
6. Jeans, J. H.: *Loc. cit.*, Chap. XII, p. 290 ff.
7. Chapman: *Phil. Trans. Roy. Soc.*, **A211**, 433, 1912; **A216**, 279, 1915; **A217**, 115, 1916; *Proc. Roy. Soc.*, **A93**, 1, 1926; *Phil. Mag.*, **48**, 593, 1926.
8. Enskog: "Kinetische Theorie der Vorgänge in Mässig Verdünnten Gasen," Inaugural dissertation, Upsala, 1917.
9. King: See Jeans, *loc. cit.*, p. 299.
10. Maxwell, J. C.: On Viscosity and Internal Friction of Air and Other Gases, in "Collected Works," vol. 2, p. 1.
11. Maxwell, J. C.: *Phil. Trans. Roy. Soc.*, p. 249, 1866.
12. Stefan, J.: *Sitzb. Akad. Wiss. Wien*, **65**, 2, 45, 1872.
13. Winkelmann: *Pogg. Ann.*, **156**, 497, 1876.
14. Sutherland: Sec. 63 of this text.
15. Boltzmann, L.: "Vorlesungen über Gastheorie," vol. I, Chaps. II and III.
16. Jeans, J. H.: "Dynamical Theory of Gases," 3d ed., 1931; Chap. VIII, p. 206, and Chap. IX, p. 231. (Dover Reprint)
17. Eucken, A.: *Phys. Z.*, **14**, 329, 1913.
18. Jeans, J. H.: "Dynamical Theory of Gases," 3d ed., p. 302.

III. DIFFUSION

70. Definition of Diffusion.—If a gas of one sort be confined in a vessel adjoining another vessel filled with a different gas at the same pressure, and if the vessels be suddenly made to communicate with each other, the first gas will slowly spread throughout the two vessels until its concentration is uniform. The other

gas will simultaneously move in such a manner as to distribute itself equally throughout the space in both vessels. This phenomenon is known as the interdiffusion of the two gases. If the attention be fixed on one gas only, the statement may be made that it diffuses into the other gas and the time rate of this process may be studied. Fixing one's attention on the one gas, it has *been assumed from experiment* that, for the steady state, the number of molecules N diffusing through a given area $dxdy$ in a time dt may be expressed by the relation

$$N_{dxdydt} = -D\frac{dN}{dz}dtdxdy.$$

In this equation, dN/dz is the rate of change in the number of molecules of the gas per unit volume (*i.e.*, the concentration) along the z-axis normal to the xy plane. D is a constant of proportionality and depends on the gases in question. The concentration gradient dN/dz is the cause of the process of diffusion and is proportional to the partial pressure gradient dp/dz of the gas. The sign is negative since the transfer takes place from higher values of N to lower ones.

Obviously, the constant D depends on the rate at which the molecules can move across the area $dxdy$ as a result of the gradient of their partial pressure p. This, as with all pressure phenomena, is obviously caused by the heat motions, and the problem then merely resolves itself into one of determining the net number of molecules moving across a given area under a concentration gradient due to their proper heat motions. The phenomenon of diffusion also occurs in liquids and solids, and in both of these the general laws are the same. As is the case in viscosity and heat conduction, the effect of the intense intermolecular forces in these latter two cases, however, complicates the problem, and the treatment that is given for the case of gases does not apply.

While fixing the attention on the molecules of one kind simplifies the analysis from the mathematical point of view, it greatly restricts the applicability of the results to the more general cases, for, unless the diffusion occur for one kind of molecules into a gas composed of molecules of the same mass velocity and free paths, the equation is incomplete. In general, then, the interdiffusion of molecules must really be treated. To this end a gas may be considered in which the pressure is everywhere the

same and which consists of two kinds of molecules, A and B, the composition varying from layer to layer along the vertical z-axis, being constant, however, parallel to the x- and y-axes. Call m_A and m_B the masses and N_A and N_B the number of the two kinds of molecules per cm^3. It is convenient to express the composition by the variable mol fraction F of A, where this may be defined as

$$F = \frac{N_A}{N_A + N_B}.$$

Then by experiment it is found that the mass of A diffusing downward across the element of area $dxdy$ of the plane $z = z_0$ in a time dt may be assumed to be given by the expression

$$d(m_A N_A)_{z_0} = -D \frac{dF}{dz} m_A N dxdydt.$$

In this treatment $N\frac{dF}{dz}$ is the same as the concentration gradient dN/dz used in the simpler case.

If, now, one considers a cylinder of base $dxdy$ and height Δz parallel to the z-axis the mass diffusing out of the cylinder in dt is given by the expression above. The mass diffusing into the cylinder at the point $z = z_0 + \Delta z$ is then given by

$$d(m_A N_A)_{z_0+\Delta z} = -m_A N dxdydt\left[D\frac{\partial F}{\partial z} + \frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right)\Delta z \right].$$

The difference of the quantities entering and leaving the cylinder gives the accumulation of molecules A in the cylinder in the time dt as

$$-m_A N dxdy\Delta z dt \frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right).$$

This quantity is also the time rate of increase of the mass of A molecules in the cylinder, that is,

$$m_A N \frac{\partial F}{\partial t} dxdy\Delta z dt.$$

Putting these two quantities equal to each other,*

$$m_A N dxdy\Delta z dt \frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right) = m_A N \frac{\partial F}{\partial t} dxdy\Delta z dt$$

* The negative sign may be neglected here, as it represents the motion only with regard to the sign of N which is not of interest in this discussion.

or $$\frac{\partial F}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial F}{\partial z}\right).$$

If D be assumed independent of z, one may write $\frac{\partial F}{\partial t} = D\frac{\partial}{\partial z}\left(\frac{\partial F}{\partial z}\right)$. This latter equation says that the rate of increase of the mol fraction of molecules with the time is the diffusion coefficient multiplied into the rate of change of the mol-fraction concentration gradient $\partial F/\partial z$ with z.

This expression is exactly the same as the Fourier[1] equation for heat conduction in a solid body. In the latter case the quantity F would be replaced by T, the temperature, and D would be replaced by h^2, the "temperature diffusivity" of the substance, where $h^2 = K/\rho c$, K being the coefficient of heat conductivity, c the specific heat, and ρ the density of the substance. Both these equations in practical application assume h and D independent of T or F. This, although not strictly true, is sufficiently correct for the solution of most problems.* Thus all the classical solutions of the Fourier heat equation may be carried over to the case of diffusion with the modifications indicated. In the present discussion, as is done practically with heat, it is often simpler to deal with cases in which a steady state has been approximated, that is, the experiments are performed in such a manner as to make $dF/dt = 0$. Then dF/dz takes on a constant value, and experimental measurement and discussion are simplified. This is the case in the simple treatment given in Sec. 71.

Some notion of the phenomenon may be gained from the table below, which gives the values of D for some of the commoner substances. The diffusion coefficients are given as the mass of the diffusing gas which crosses 1 cm^2/sec. when there is unit mass concentration gradient present at the point (*i.e.*, when

* The variation of D with F, when it occurs, gives rise to an apparent mass motion of the gas. This may be seen by carrying out the differentiation, assuming D to be a function of F and hence of z.

$$\frac{\partial F}{\partial t} = D\frac{\partial^2 F}{\partial z^2} + \frac{\partial D}{\partial z}\frac{\partial F}{\partial z}.$$

The increase of $\partial F/\partial t$ due to the variation of D with F is that which would result if the gas were to have a mass motion with a velocity $w_0 = -\frac{dD}{dz}$ for the quantity dD/dz has the dimensions L/T. That this is so will be seen in Sec. 72.

$\frac{d(m_A N_A)}{dz}$ = 1 gram per cm^3 per cm along z). In fact it is immaterial whether the quantity diffusing is expressed as the mass of gas or the number of molecules as long as the concentration gradient is expressed in the same unit or quantity; for in the expression $D = \frac{N_{dxdydt}}{(dN/dz)dxdydt}$ the quantity N cancels out dimensionally.

Gas diffusing	Gas diffused into	D	t, in degrees centigrade
H_2	O_2	0.677	0
H_2	CO_2	0.538	0
O_2	N_2	0.171	0
O_2	H_2	0.722	0
CO_2	N_2O	0.15	0
C_2H_5OH	Air	0.102	0
C_2H_5OH	CO_2	0.068	0
C_2H_5OH	H_2	0.378	0

Substance diffusing	Solute	D for 1 sec.
Glycerine	Water	7.83×10^{-6}
Acetamide	Water	10.4×10^{-6}
Mannose	Water	5.62×10^{-6}
HCl	Water	2.66×10^{-5}
NaCl	Water	1.28×10^{-5}
$NaCH_3CO_2$	Water	9.02×10^{-6}

In solids the rate is far slower yet, and it is interesting to note the large difference in the values of D for gases and for solutions.

71. The Theory of Self-diffusion of Molecules.—Consider molecules of a certain mass and diameter diffusing into a gas of molecules of similar mass and diameter. The phenomenon is known as *self-diffusion.* Assume that a uniform rate of flow has been established, that is to say, that $dN/dt = 0$. Under these conditions the molecules have reached an equilibrium state, and a linear concentration gradient dN/dz along the z-axis has been obtained. Assume, further, that the concentration decreases from above downward. The state pictured would be nearly achieved if molecules from an indefinitely large vessel of CO_2

were diffusing along a long tube into an indefinitely large chamber of N_2O molecules. After some time the rate of change in concentration at one point in the tube would have ceased and the concentration at any point z above an arbitrarily chosen xy plane normal to the tube would be given by $N + z\frac{dN}{dz}$, where N is the number of molecules per cm^3 at $z = 0$, or at the xy plane. Below the plane at a point z the number of molecules would be $N - z\frac{dN}{dz}$. Consider now an area $dxdy$ in the xy plane. At L cm above it there will be $N + L\frac{dN}{dz}$ molecules. If L is the average free path, one-sixth of the molecules moving with a velocity $\bar{c}$ will have velocities directed so as to pass down through $dxdy$ on their next free path. The number of molecules in a layer dL in height and of base $dxdy$ is $dxdydL\left(N + L\frac{dN}{dz}\right)$. These are the molecules which will in the next path pass through $dxdy$ downward. Now the length dL may be represented by the molecules traveling with a velocity $\bar{c}$, which in a time dt pass through a distance L. Hence the number of molecules passing from the volume $dxdydL$ or $dxdy\bar{c}dt$ through the area $dxdy$ as a result of the concentration gradient in the time dt will be the number that lie in this cylinder multiplied by the fraction which have velocities $\bar{c}$ in the direction z such that they will pass through $dxdy$, that is,

$$N_{dt\downarrow} = -\frac{1}{6}dxdy\bar{c}dt\left(N + L\frac{dN}{dz}\right),$$

the minus sign denoting that the molecules are passing from higher values of N to lower values. In a similar manner, the number of molecules passing from the layer L below xy upwards through $dxdy$ in dt will be

$$N_{dt\uparrow} = +\frac{1}{6}dxdy\bar{c}dt\left(N - L\frac{dN}{dz}\right).$$

The total net transfer of molecules through $dxdy$ will be

$$N_{dt} = N_{dt\downarrow} + N_{dt\uparrow}$$

or

$$N_{dt} = -\frac{1}{3}dxdy\bar{c}dtL\frac{dN}{dz}.$$

The number passing per unit time will then be $N_{dxdy} = N_{dt}/dt$, whence the number of molecules diffusing through $dxdy$ per second will be

$$N_{dxdy} = -\frac{1}{3}dxdy\frac{dN}{dz}\bar{c}L.$$

But this has been shown by experiment to be given by

$$N_{dxdy} = -D\frac{dN}{dz}\,dxdy.$$

Whence

$$D = \frac{1}{3}\,\bar{c}L.$$

This is the coefficient of diffusion as defined for the simple case.

Since $\eta = \frac{1}{3}Nm\bar{c}L$ it follows at once that $D = \eta/Nm$. But mN is ρ, the density, so that one may write $D = \eta/\rho$.

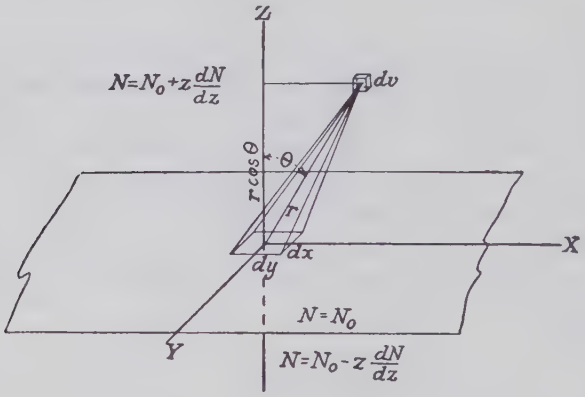

FIG. 43.

The same expression may be derived in a more rigorous fashion, taking into account the distribution of free paths and velocities. Assume, as before, that the steady state has been reached and that the concentration above and below the xy plane may be represented by $N + z\frac{dN}{dz}$, and $N - z\frac{dN}{dz}$. Consider an element of volume dv above the xy plane at a distance r from the area $dxdy$, such that the line from dv to $dxdy$ makes an angle θ with the normal to $dxdy$ (Fig. 43). Thus $z = r\cos\theta$. Each of the molecules in dv has a mean free path L and a velocity c, then each molecule *starts a new free path* c/L times a second. Now in dv

there are $dv \frac{4}{\alpha^3\sqrt{\pi}} c^2 e^{-\frac{c^2}{\alpha^2}} dc\left(N + r \cos\theta \frac{dN}{dz}\right)$ molecules with a velocity between c and $c + dc$. Of these, the number in a cone of base $dxdy \cos\theta$ and height r will have velocities directed towards $dxdy$, that is,

$$\frac{dxdy \cos\theta}{4\pi r^2} \frac{4}{\alpha^3\sqrt{\pi}} \frac{c^3}{L} e^{-\frac{c^2}{\alpha^2}} dc dv\left(N + r \cos\theta \frac{dN}{dz}\right)$$

molecules will start for $dxdy$ per second. But, of these, only the fraction $e^{-\frac{r}{L}}$ will have paths exceeding r and will, accordingly, be able to pass through $dxdy$ without impact. Hence the number of molecules from dv passing downward through $dxdy$ per second will be

$$N_{dv\downarrow} = \frac{dxdy \cos\theta dv}{4\pi r^2} e^{-\frac{r}{L}} \frac{4}{\alpha^3\sqrt{\pi}} \frac{c^3}{L} e^{-\frac{c^2}{\alpha^2}} dc\left(N + r \cos\theta \frac{dN}{dz}\right).$$

Expressing dv in terms of the polar coordinates, $dv = (dr)(rd\theta)(r \sin\theta\, d\phi)$, one has the number $N_{dv\downarrow}$ given as

$$N_{dv\downarrow} = \frac{dxdy}{\pi L} \frac{c^3}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} dc e^{-\frac{r}{L}} dr \cos\theta \sin\theta d\theta d\phi \left(N + r \cos\theta \frac{dN}{dz}\right).$$

In a similar fashion the number passing from a volume dv below the xy plane may be found to be

$$N_{dv\uparrow} = \frac{dxdy}{\pi L} \frac{c^3}{\alpha^3\sqrt{\pi}} e^{-\frac{c^2}{\alpha^2}} dc e^{-\frac{r}{L}} dr \cos\theta \sin\theta d\theta d\phi \left(N - r \cos\theta \frac{dN}{dz}\right).$$

These expressions must now each be integrated for c from 0 to ∞, for r from 0 to ∞, for θ from 0 to $\pi/2$, and for ϕ from 0 to 2π to give the total numbers of molecules of all velocities passing through $dxdy$ from the volumes above and below the xy plane. Integration gives

$$N_{\downarrow} = \left\{\frac{N\bar{c}}{4} + \frac{dN}{dz} \frac{\bar{c}}{6} L\right\} dxdy.$$

$$N_{\uparrow} = \left\{\frac{N\bar{c}}{4} - \frac{dN}{dz} \frac{\bar{c}}{6} L\right\} dxdy.$$

To get the total number passing through $dxdy$ these expressions would have to be added, remembering that $N_{\downarrow}$ has the negative sign, for the molecules are moving from a region of higher

concentration to one of lower concentration. Hence $N_{dxdy} = -N_{\downarrow} + N_{\uparrow}$

or $$N_{dxdy} = -\frac{1}{3}\bar{c}L\frac{dN}{dz}\,dxdy.$$

Since, by experiment for the steady state,

$$N_{dxdy} = -D\frac{dN}{dz}\,dxdy,$$

then at once $D = \frac{1}{3}\bar{c}L$ which was the result arrived at before in a much more elementary fashion. It might be added in passing that had dN/dz been 0, N_{dxdy} would have been 0. For this case $N_{\downarrow}$ equals $N_{\uparrow} = N\bar{c}/4$, that is, one would have found the number of molecules striking a cm^2 per second from above or below to be $N\bar{c}/4$. This result was obtained in Sec. 40.

72. The Theory of Interdiffusion.—In this section the more general treatment of the interdiffusion of two gases A and B will be taken up where the masses of the molecules A and B are not equal. In what follows use will be made of the mol fraction, and the notation in the latter part of Sec. 70 will apply.

As the temperature is constant throughout the gases the *most probable speeds* of the A and B molecules α_A and α_B will be different as a result of equipartition of energy. Thus

$$m_A\alpha_A^2 = m_B\alpha_B^2.$$

It will be assumed that the variations of F, the mol fraction of A, with z are so small over a free path that the distribution of velocities of the two kinds of molecules may be considered Maxwellian.

Although the molecular density remains constant in pure diffusion, since the total pressure is everywhere the same, the changing composition means a change in the mass density. This means that there is a mean *mass* velocity of the gas in the direction of diffusion. Let this velocity, which is very small, be denoted by w_0. It is a *mass* velocity of the molecules along the z-axis of coordinates, diffusion taking place along the z-axis as assumed in Sec. 71. Owing to the presence of this mass-motion velocity, w_0, the number of molecules having components along the various axes is no longer the same. Out of N molecules of the type A, $\frac{N}{\alpha_A\sqrt{\pi}}e^{-\frac{u^2}{\alpha_A^2}}\,du$ will have velocities between u and

$u + du$, and $\frac{N}{\alpha_A\sqrt{\pi}} e^{-\frac{v^2}{\alpha_A^2}} dv$ molecules will have velocities between v and $v + dv$, but $\frac{N}{\alpha_A\sqrt{\pi}} e^{-\frac{(w-w_0)^2}{\alpha_A^2}} dw$ molecules will have velocities between w and $w + dw$ owing to the component w_0, for the velocity w is composed of the mass velocity w_0 and the translational heat velocity $w - w_0$. Maxwell's law applies to the translational velocities only, and these must be included. This will be $w - w_0$ for the positive component, and $-w + w_0$ for the negative component. Both terms represent the difference in two velocities. The sign of the whole expression is immaterial, since the term is squared. The number of molecules having velocity components between u and $u + du$, v and $v + dv$, and w and $w + dw$ simultaneously is, then,

$$\frac{N}{\alpha_A^3\pi^{3/2}} e^{-\frac{[u^2+v^2+(w-w_0)^2]}{\alpha_A^2}} dudvdw.$$

At a point in the gas where the mol fraction has a value F there will be F times the number of A molecules with velocities lying within the limits specified above. Of these, those lying in a volume, $w\,dtdxdy$ will pass through an area $dxdy$ in a time dt. The total number which will pass through this area in dt requires integration from $-\infty$ to $+\infty$ for the u- and v-components, and from 0 to ∞ for the w-component if only the transfer from above downward is regarded. For the net transfer the integration would have to be carried from $-\infty$ to $+\infty$ for the w-component as well. Thus the net number of A molecules crossing $dxdy$ in the plane $z = z_0$ in the time dt is given by

$$\frac{N dtdxdy}{\alpha_A^3\pi^{3/2}} \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} Fwe^{-\frac{u^2+v^2+(w-w_0)^2}{\alpha_A^2}} dudvdw.$$

This expression will not vanish for two reasons: First, because of the component of streaming motion w_0, and, second, because F has different values on the two sides of the xy plane. Now the molecules which pass through the area $dxdy$ are only those that had their last collision a free path away, that is, only those molecules which started anew from a collision L cm away will pass through $dxdy$. Thus the value of F chosen is the one which corresponds to the scene of the last impact. If the molecular path makes an angle θ with the z-axis, this distance will be L

cos θ distant from z_0. For a steady state or where F does not change rapidly with the distance, one may write

$$F = F_0 + \left(\frac{dF}{dz}\right)_0 L \cos\theta.$$

Moreover, since w_0 is small compared with α_A, one may write $e^{-\frac{(w-w_0)^2}{\alpha_A{}^2}} = \left(1 + \frac{2ww_0}{\alpha_A{}^2}\right)e^{-\frac{w^2}{\alpha_A{}^2}}$. With these substitutions, the expression for the net number of A molecules crossing *unit area* in a time dt becomes:

$$\frac{N dt}{\alpha_A{}^3\pi^{3/2}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left[F_0 + L\cos\theta\left(\frac{\partial F}{\partial z}\right)_0\right]w\left(1 + \frac{2ww_0}{\alpha_A{}^2}\right) e^{-\frac{u^2+v^2+w^2}{\alpha_A{}^2}} du dv dw.$$

This may be transformed to an expression in the polar coordinates c, θ, and ϕ, as in Sec. 34, and then becomes

$$\frac{N dt}{\alpha_A{}^3\pi^{3/2}}\int_0^{\infty} dc\int_0^{2\pi} d\phi\int_0^{\pi}\left[F_0 + L\cos\theta\left(\frac{\partial F}{\partial z}\right)_0\right]\left(1 + 2\frac{w_0 c}{\alpha_A{}^2}\cos\theta\right) c^3 e^{-\frac{c^2}{\alpha_A{}^2}}\sin\theta\cos\theta d\theta.$$

Integration with respect to ϕ gives the factor 2π. Multiplication and neglect of small terms of higher order than the first one give

$$\frac{2N dt}{\alpha_A{}^3\sqrt{\pi}}\int_0^{\infty} dc\int_0^{\pi}\left[F_0 + 2F_0\frac{w_0 c}{\alpha_A{}^2}\cos\theta + L\cos\theta\left(\frac{\partial F}{\partial z}\right)_0\right]c^3 e^{-\frac{c^2}{\alpha_A{}^2}} \sin\theta\cos\theta d\theta.$$

Integration with respect to θ yields

$$\frac{4N dt}{3\alpha_A{}^3\sqrt{\pi}}\int_0^{\infty}\left[2F_0\frac{w_0 c}{\alpha_A{}^2} + L\left(\frac{\partial F}{\partial z}\right)_0\right]c^3 e^{-\frac{c^2}{\alpha_A{}^2}} dc.$$

Assuming L independent of c, integration leads to the result

$$N dt\left\{F_0 w_0 + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right\}.$$

This is the net number of A molecules crossing the plane $z = z_0$ in the direction of the gradient. In a similar manner the expression for the B molecules diffusing from below the $z = z_0$ plane upwards may be found to be

$$Ndt\left\{(1 - F_0)w_0 - \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_B L_B\right\}.$$

Here the concentration of B molecules is given by $(1 - F_0)$, where F_0 is the mol fraction of A molecules, and the minus sign comes from the fact that the concentration of B molecules decreases as z increases.

Since the molecular density must remain constant everywhere, the total number of molecules crossing the plane must be 0, that is,

$$- Ndt\left\{(1 - F_0)w_0 - \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_B L_B\right\}$$

must equal

$$Ndt\left\{F_0 w_0 + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right\},$$

whence

$$-w_0 = \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \left\{\bar{c}_A L_A - \bar{c}_B L_B\right\}.$$

This value of w_0 may be substituted into the expression for the number of A molecules diffusing through unit area in the $z = z_0$ plane in the time dt, which is

$$Ndt\left\{F_0 w_0 + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right\}$$

and gives the number at once in terms of the mol fractions of A molecules, the concentration gradient, and the free paths and average velocities of A and B molecules, to wit

$$Ndt\left[-F_0 \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \left\{\bar{c}_A L_A - \bar{c}_B L_B\right\} + \frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \bar{c}_A L_A\right]$$
$$= \frac{1}{3} Ndt\left(\frac{\partial F}{\partial z}\right)_0 \left[(1 - F_0)\bar{c}_A L_A + F_0 \bar{c}_B L_B\right].$$

The mass of A molecules crossing an area $dxdy$ in unit time is then merely this quantity multiplied by m_A and $dxdy$, whence

$$d(m_A N_A)_{dxdydt} = -\frac{1}{3} Ndt\left(\frac{\partial F}{\partial z}\right)_0 dxdy\left[(1 - F_0)\bar{c}_A L_A + F_0 \bar{c}_B L_B\right] m_A.$$

But by definition

$$d(m_A N_A)_{dxdydt} = -DNdt\left(\frac{\partial F}{\partial z}\right)_0 dxdy m_A.$$

Therefore

$$D = \frac{1}{3}\left[(1 - F_0)\bar{c}_A L_A + F_0 \bar{c}_B L_B \right].$$

This is the classical expression for the interdiffusion of two gases in terms of their average speed and mean free paths.

It is of interest to notice in passing that the mass motion of the gas was given by

$$w_0 = -\frac{1}{3}\left(\frac{\partial F}{\partial z}\right)_0 \left\{ \bar{c}_A L_A - \bar{c}_B L_B \right\}.$$

If the expression for D just found is differentiated with respect to F,

$$\frac{dD}{dF} = -\frac{1}{3}\left[\bar{c}_A L_A - \bar{c}_B L_B \right]$$

or

$$w_0 = \left(\frac{\partial F}{\partial z}\right)_0 \frac{\partial D}{\partial F},$$

which agrees with the formula found on purely hydrodynamic grounds in Sec. 70.

Since the viscosity of a gas is given by $\eta = \frac{1}{3}\rho\bar{c}L$, the expression for interdiffusion of the gases may be written as

$$D = F_0 \frac{\eta_B}{\rho_B} + (1 - F_0)\frac{\eta_A}{\rho_A}.$$

73. Criticism of Transfer Theory.—This section contains a discussion of the theoretical results obtained in preceding sections, together with a statement of some results of theoretical investigations on diffusion, the details of which are too advanced for inclusion in this book.

For simplicity, in the preceding discussion L was treated as a constant and placed in front of the integral sign. A more exact treatment would require that the expression for L_c, the mean free path of a molecule of speed c (Sec. 39) be used, and that the integration using this value be carried out. In Sec. 39 the value of L_c was found for a molecule of speed c moving in a pure gas. To be applicable in the foregoing derivation, it would be necessary to generalize the expression to the case of a gas consisting of two kinds of molecules. The results of such a generalization lead to a complicated definite integral which must be evaluated for each value of the mol fraction F. Tait[2] has carried the analysis to the point of

setting up the very complicated integrals involved, but they have seemingly never been computed, so that one cannot say how this refinement would affect the theory.

The correction becomes considerably simpler when the gases A and B have the same molecular weight and the same diameter. In this case the most probable speeds α_A and α_B are equal, as are also the collision frequencies Z. Then L_c is given by the expression of Sec. 39. Using this in the theory, it is seen that the resulting integral is the same as that occurring in the viscosity theory (Sec. 59), so that the result there given is applicable here. One has, then,

$$D = \frac{1}{3} \cdot \bar{c}L \cdot 1.051$$

as the coefficient of diffusion for two gases of equal molecular weight and diameter. The L here used is the Maxwell free path. The application of this correction does not change the relation $D = \eta/\rho$, since it affects both the diffusivity and the viscosity by the same amount.

The equation for interdiffusion gives

$$D_i = \frac{1}{3}[(1 - F_0)\bar{c}_A L_A + F_0 \bar{c}_B L_B] = \frac{1}{3} \frac{(N_B \bar{c}_A L_A + N_A \bar{c}_B L_B)}{N_B + N_A}.$$

It is clear that, if either N_A or $N_B = 0$, one has $D_i = \frac{1}{3}\bar{c}_A L_A$ or $D_i = \frac{1}{3}\bar{c}_B L_B$, which are the expressions for self-diffusion of molecules A and B in gases of their own species. Now assume gas A to be H_2 and gas B to be CO_2 in which $\bar{c}_A/\bar{c}_B$ vary in the ratio $\sqrt{m_B/m_A}$, where m_A and m_B are the molecular weights of H_2 and CO_2. Furthermore L_A and L_B are widely different. In a mixture of A and B, L_A and L_B vary continuously according to the equations of Sec. 38 on mean free paths in mixtures. Jeans shows that L_A for gas A molecules moving in 100 per cent gas B, and L_B moving in 100 per cent gas A, vary in the ratio $L_A/L_B = \sqrt{m_B/m_A}$. Thus in the extreme cases of interdiffusion, $D_{AB}/D_{BA} = m_B/m_A$, which may have very large values as in the case of CO_2 and H_2 where it is 22:1. Hence the value of D_i in a mixture of varying constitution should vary over wide limits. This is found by experiment to be incorrect as the table on page 274 shows. This discrepancy between Meyer's classical

equation for interdiffusion (see Sec. 72), which is the only type of diffusion in gases open to experimental investigation, and experiment is very great. The discrepancy is in part due to the neglect of the phenomenon which Jeans calls persistence of velocities. As was shown in Sec. 59 for viscosity, the correction for persistence makes $\eta = \frac{1}{3(1 - \frac{1}{2}\theta)} mN\bar{c}L$. In the case of self-diffusion D the correction is $D = \frac{1}{3(1 - \theta)} \bar{c}L$; whence $D = \frac{1 - \frac{1}{2}\theta}{1 - \theta} \frac{\eta}{\rho}$. If $\theta = 0.406$ as Jeans[14] evaluates it, the value of D becomes $1.34\,\eta/\rho$.

For interdiffusion the correction for persistence becomes much more complicated. Jeans shows that the quantity θ depends on the masses of the molecules A and B so that θ_{AB} is very different from θ_{BA}. This value of θ for molecules colliding with their own kind and θ_{AB} and θ_{BA} for collisions between molecules of masses m_A and m_B must be put into the expressions for L_{AB} and L_{BA} which occur in the equation for interdiffusion, as multipliers of $\sigma^2{}_A$, $\sigma^2{}_B$, and $\sigma^2{}_{AB}$, the squares of the collision diameters. Putting in these corrections it turns out that the ratio of D_{AB} and D_{BA} for self-diffusion in a gas composed of molecules of a different kind becomes $\frac{D_{AB}}{D_{BA}} = \frac{1 + \alpha_{BA}}{1 + \alpha_{AB}}$ instead of $\frac{D_{AB}}{D_{BA}} = \frac{m_B}{m_A}$ as before. Here α_{BA} and α_{AB} are the values of α in Jeans' expression for persistence in which α/c are expressed in terms of the ratios of the masses m_A and m_B involved in collision. As the extreme values for α are 0 and $\frac{1}{3}$, the greatest range possible for the ratio of $D_{AB}/D_{BA} = \frac{4}{3}$ which is much less than that predicted by Meyer.

Stefan[11] and Maxwell[3,15] proceeded to the study of the problem of interdiffusion in a somewhat different fashion. They recognized the importance of the free path in the diffusion phenomenon. They considered the mean free path of a gas molecule A in a gas composed of A and B molecules in the form of the expression on page 99 in which the velocities were replaced by the equivalent mass, to wit

$$L_{AB} = \frac{1}{\sqrt{2}\pi N_A \sigma_A{}^2 + \pi N_B \sigma_{AB}{}^2 \sqrt{1 + \frac{m_A}{m_B}}}.$$

In looking at this from the point of view of interdiffusion, they disregarded the effect of the term due to collisions of A molecules with A molecules and in the L_{BA} of the collisions of B molecules with B molecules so that they called

$$L_A = \frac{\bar{c}_A}{\sqrt{\bar{c}_A^2 + \bar{c}_B^2}\pi N_A \sigma_{AB}^2} \quad \text{and} \quad L_B = \frac{\bar{c}_B}{\sqrt{\bar{c}_A^2 + \bar{c}_B^2}\pi N_B \sigma_{AB}^2}.$$

These values were then placed in the expression for D_i, the coefficient of interdiffusion. This gave

$$D_i = \frac{\sqrt{\bar{c}_A^2 + \bar{c}_B^2}}{3\pi(N_A + N_B)\sigma_{AB}^2}.$$

For molecules of equal size and mass this gives the coefficient of self-diffusion as $D = \frac{2}{3}\frac{\bar{c}}{\sqrt{2}\pi N\sigma^2}$, and, if Chapman's exact expression for η, the coefficient of viscosity, $\eta = 0.499\frac{\rho\bar{c}}{\sqrt{2}\pi N\sigma^2}$, is used, $D = 1.336\frac{\eta}{\rho}$ in agreement with the persistence of velocity equation. It is further to be noted that D_i is in this case completely independent of composition. Actually D_i is not accurately independent of composition but varies in the order of a few per cent (*i.e.*, 0 to 8). Thus it is clear that one must proceed as in the case of η and K to take account of the more accurate general equations of Chapman and Enskog; and, for the same reason, that with changes in concentration one cannot properly assume Maxwell's distribution of velocities.

Both by Boltzmann's[4] method and that of Maxwell[16] for a repulsive law of force, $f = Gr^{-n}$ where $n = 5$, solutions which are exact were obtained. These solutions are as good as those obtained by the classical procedure. For Maxwell's case of $n = 5$ the coefficient of self-diffusion was $D = 1.504\frac{\eta}{\rho}$. These methods, as in the case of η and K, are not applicable to real gases as the real laws of force are of higher power than the inverse fifth. More complete results were found by Chapman[5] and Enskog[6] for different values of the repulsive force, ranging from $n = 5$ to $n = 17$, and for $n = \infty$ (elastic spheres) to a second approximation. Chapman finds for the self-diffusion of elastic spheres which gives the highest value of ϵ, $D = \epsilon\frac{\eta}{\rho} = 1.200\frac{\eta}{\rho}$.

For the case of interdiffusion Chapman and Enskog have carried out the calculations to a second approximation.

The chief interest in these expressions is the result obtained in the question of the change of D_i with concentration. For elastic spheres Enskog found

$$\frac{D_{N_A=0}}{D_{N_B=0}} = \frac{1 + \dfrac{m_B^2}{12m_B^2 + 16m_Am_B + 30m_A^2}}{1 + \dfrac{m_A^2}{12m_A^2 + 16m_Am_B + 30m_B^2}},$$

to a second approximation. For the case $m_B/m_A = 10$, *e.g.*, for the gas neon in hydrogen, the values found for the ratio above are

Meyer's theory	10.00
Meyer's theory with persistence correction	1.324
Chapman-Enskog	1.072

This last result for the effect of concentration as well as the value of ϵ which ranges from 1.2 to 1.504, depending on the law of force, turns out to be in good agreement with the experimental results obtained. Thus again it is seen that by these rigorous but tedious and complex general methods the problem is successfully solved to the extent which a knowledge of the laws of force permits.

74. Measurement of Gaseous Diffusion.—The first measurements of gas diffusion which were conducted in such a way that D could be evaluated from the data were made by Loschmidt[8] in 1870. The method he used is virtually the same as that used in all subsequent measurements of gas diffusion. He used a glass tube 97.5 cm long and 2.6 cm in diameter which was held in a vertical position. At its center it was divided into two parts by a partition. Initially, the top half was filled with the lighter of the two gases to be studied and the bottom half with the heavier. Then the partition between them was carefully removed and the diffusion began. At a measured time later the partition was put back in place again. The contents of the two halves of the tube were then analyzed, and from the change in composition the value of the coefficient of diffusion was inferred.

It is desirable to give an account of the method in some detail in order to see what the experiments teach. The theory will be developed on the assumption that D does not depend on the

composition of the gas at the place where the diffusion is taking place. Moreover, it will be remembered that when the diffusion equation was developed it was *assumed* that the mass of gas crossing unit area in unit time was simply proportional to the rate of change of the composition of the gas across that plane. Let it be supposed that a series of experiments like those just outlined were carried out, starting with the same gases but allowing different times to elapse before the partition was closed. If, now, the values of D inferred from each experiment in such a set should prove to be equal, the experiments would have confirmed the hypotheses made in the theory. If D should vary, however, it might be due to the fact that D is a function of the composition or to a more fundamental error coming from the assumption that the transfer of mass across a plane is not simply proportional to the composition gradient. The complete critical discussion of the experiments and their significance for these alternatives cannot be given in detail. The results will be given in the next section, where the measurements of D are summarized.

The theory of the Loschmidt method for the measurement of diffusion calls for the solution of the complete diffusion equation with appropriate boundary conditions. Let the length of the tube be a. Take the origin of x at the bottom so that the tube runs from $x = 0$ to $x = a$. At the initial instant, $t = 0$, assume the mol fraction F of A to be 1 from $x = 0$ to $x = a/2$ (*i.e.*, let it be assumed that there be only A molecules in the lower half and that above this point, from $x = a/2$ to $x = a$, there be none), also let it be assumed that there be only molecules of the B type in the upper half of the tube. Since no diffusion takes place through the ends of the tube, it follows also that

$$\frac{\partial F}{\partial x} = 0 \text{ at } x = 0 \text{ and } x = a \textit{ at all times.}$$

The solution of this problem for the conduction equation of Sec. 70 when $dF/dt \neq 0$ is well known from the classical work in heat and is given in detail in works on partial differential equations, such as Byerly's[9] "Fourier Series and Spherical Harmonics." The solution is given in the form of a Fourier series and is as follows:

$$F = \frac{1}{2} + \frac{2}{\pi} \sum_{n=1}^{n=\infty} \frac{1}{n} \sin \frac{n\pi}{2} e^{-Dt\left(\frac{n\pi}{a}\right)^2} \cos \frac{n\pi x}{a}.$$

This infinite series expresses the mode of variation of F with the time at each place in the tube. In the experiments the partition is replaced at the time t and the composition of the gas in the upper and lower halves of the tube determined by analysis. What is measured is the average value of F in each half of the tube. The measurements give F_L and F_u, the average values of F, in the lower and upper parts respectively. The averages can be computed in terms of D and t from the series by the formulæ:

$$\bar{F}_L = \frac{2}{a}\int_0^{\frac{a}{2}} F\,dx, \qquad \bar{F}_u = \frac{2}{a}\int_{\frac{a}{2}}^{a} F\,dx.$$

This yields for the two averages

$$\bar{F}_L = \frac{1}{2} + \frac{4}{\pi^2}\sum\frac{1}{n^2}\sin^2\frac{n\pi}{2}\,e^{-Dt\left(\frac{n\pi}{a}\right)^2}$$

$$\bar{F}_u = \frac{1}{2} - \frac{4}{\pi^2}\sum\frac{1}{n^2}\sin^2\frac{n\pi}{2}\,e^{-Dt\left(\frac{n\pi}{a}\right)^2}.$$

The difference in the mol fractions is, then,

$$\bar{F}_L - \bar{F}_u = \frac{8}{\pi^2}\left[e^{-\frac{\pi^2}{a^2}Dt} + \frac{1}{9}e^{-\frac{9\pi^2 Dt}{a^2}} + \frac{1}{25}e^{-\frac{25\pi^2 Dt}{a^2}} + \cdots\right].$$

In this expression the terms after the first three are so small for moderate values of t that they are quite negligible. It will be observed that the analysis of the contents of but one of the tubes is necessary, since if one is known the other follows from it directly. The manner in which D is to be computed from the above equation when $\bar{F}_L$, $\bar{F}_u$, a, and t are known is rather involved and can be carried out only by successive approximations or graphical methods. In experimental work the times are such that the first three terms of the series only are necessary.

V. Obermayer[10] has given a table of values of $\bar{F}_L - \bar{F}_u$ computed from the series which greatly facilitates the evaluation of D from given data.

The table shown on page 271 is abridged from that of V. Obermayer. It refers to a tube for which $a = 86.62$ cm.

Stefan[11] employed another method of measuring diffusion. In it the gas is simply placed in a vertical cylindrical vessel. At the initial instant one end of the vessel (the upper one if the gas is heavier than air) is opened. After a measured time the

cylinder is closed and the contents analyzed. The theory of this method proceeds along similar lines to that of the Loschmidt method. The diffusion equation must be solved with appropriate boundary conditions. If a is the length of the tube, the conditions assumed by Stefan are, at $t = 0$, $F = 1$ for $0 < x < a$; at all times, $\partial F/\partial x = 0$ for $x = 0$ and $F = 0$ at $x = a$. This last condition corresponds to the assumption that the gas escaping

DIFFERENCE IN MOL FRACTION AS FUNCTION OF Dt

Dt	$\bar{F}_L - \bar{F}_u$	Dt	$\bar{F}_L - \bar{F}_u$
0.00	1	0.06	0.368
0.01	0.738	0.07	0.323
0.02	0.632	0.08	0.283
0.03	0.549	0.09	0.248
0.04	0.480	0.10	0.218
0.05	0.420		

from the cylinder at the mouth diffuses outward in the three directions away from the mouth so rapidly that the concentration is always zero at the mouth. This is, of course, not exactly correct but requires a small end correction, *i.e.*, the actual accumulation of gas around the end makes the tube act as if it were slightly longer than it actually is. The theory of this correction does not seem to have been developed. It seems that the Loschmidt method is capable of greater accuracy than that of Stefan.

As was mentioned earlier in this section, if the assumptions leading to the differential equation of the diffusion are correct, the values of D obtained in a series of experiments should not depend on the period of time over which diffusion takes place. Obermayer finds, however, small deviations of this sort such that, using the Loschmidt method, short periods of time invariably yield smaller values of the diffusivity than do longer periods of time. This led him to the conclusion that the mass transfer is not strictly proportional to the composition gradient but is slightly less than proportionality would require for the large values of the composition gradient which occur during the first part of the experiments. All of these deviations are less than 4 per cent of the mean value of D. They do not seem to have been given theoretical discussion.

In the measurements made by students at Halle to determine the amount of dependence of D on the composition of the gas mixture, the Loschmidt method was employed in a slightly modified form. It is interesting to note that, as but slight dependence on the composition ratio was expected, these workers used the solution of the differential equations which assume D constant. This was necessary since the equations with D variable do not yield to solution. The work was so arranged that the composition did not vary much in an experiment, so the assumed constancy of D in the treatment is probably fairly correct. In some measurements, instead of putting pure A in one-half of the tube and pure B in the other, pure A was allowed to diffuse against a mixture of A and B of known initial composition. From such data, values of D were obtained as a function of the mean composition of the diffusing mixture. In other experiments the upper half of the tube was further subdivided into two equal parts and computations of the diffusivity based on analysis of all three compartments.

75. Experimental Results on Diffusion.—The measurement of diffusivity of gases may afford several crucial tests of the kinetic theory of gases and also yields valuable data on the size of molecules. The main result of the theory is that the diffusivity of a mixture of two gases is given by:

$$D = \epsilon\left[F\frac{\eta_B}{\rho_B} + (1 - F)\frac{\eta_A}{\rho_A}\right]$$

or by

$$D = \frac{\epsilon}{3}[FL_B\bar{c}_B + (1 - F)L_A\bar{c}_A],$$

in which ϵ is a numerical factor whose value is between 1.000 and 1.500 on various assumptions, F is the mol fraction of A, η and ρ are the viscosities and densities of the two gases involved, while L_A, L_B and $\bar{c}_A$, $\bar{c}_B$ are the mean free paths and average thermal velocities. Thus the theory predicts, for a given value of F, that the diffusivity should vary with temperature and pressure in the same way as do the ratios η/ρ for the two gases. Since L_A and L_B are proportional to $1/p$, and to T *at constant pressure*, and $\bar{c}_A$ and $\bar{c}_B$ are proportional to $\sqrt{T}$, D should be proportional to the $\frac{3}{2}$ power of the absolute temperature and inversely proportional to the pressure. The accuracy of the

measurements in this field is not so great as for the related effects of viscosity and heat conduction. From the experimental results, taken at pressures around atmospheric and at temperatures near normal room temperature, it may be said that the diffusivity varies inversely as the pressure and as a power of the absolute temperature between 1.75 and 2.

In the discussion of viscosity it was seen that η, by the simple theory, varied as $T^{1/2}$ and not at all with p. Moreover, if the perfect gas laws are applicable, ρ varies as T^{-1} at constant pressure and as p. Putting these together, one has that on simple theory the diffusivity should vary as $T^{3/2}$ and as p^{-1}. The observed exponent for the variation is somewhat greater, as was just stated, and this is consistent with the fact that η actually varies with T according to a higher power than $T^{1/2}$. This more rapid increase in the case of viscosity was explained by Sutherland (Sec. 63) in terms of the effect on the mean free paths of attracting forces between the molecules. A similar analysis might be developed for the theory of diffusion, but it should be observed that it would be more complicated owing to the necessity of taking into account the attraction of A molecules on each other; that of A molecules on B molecules, and finally of B molecules on each other.

The next point on which it is interesting to compare theory and experiment is that of the variation of the diffusivity with the composition of the gas mixture. According to the simple theory, there should be a linear dependence on the mol fraction which is rather large when the values of $L\bar{c}$ for the two gases are quite different. On the other hand, according to a kinetic theory of diffusion developed by Stefan[11] and Maxwell, which was outlined on page 266, the result is obtained that the diffusion should be independent of the composition and that the value should be

$$D = 1.336\frac{\eta}{\rho}.$$

The investigation of the dependence of D on composition was made the subject of a series of doctors' dissertations by R. Schmidt (1904), O. Jackmann (1906), R. Deutsch (1907), and A. Lonius (1909), at Halle. The results of all this work are summarized in a paper by Lonius.[12] The following table, from this paper, summarizes the results:

DEPENDENCE OF D ON COMPOSITION

Gases		F	D	Observer
A	B			
O_2	H_2	0.5	0.27335	Jackmann
		0.252	0.27609	Jackmann
N_2	H_2	0.5	0.26565	Jackmann
		0.235	0.26830	Jackmann
O_2	N_2	0.5	0.073035	Jackmann
		0.467	0.073332	Jackmann
O_2	H_2	0.25	0.27616	Deutsch
		0.5	0.28003	Deutsch
		0.75	0.28934	Deutsch
CO_2	H_2	0.25	0.21351	Deutsch
		0.5	0.21774	Deutsch
		0.75	0.22772	Deutsch
Ar	He	0.5	0.25405	Schmidt
		0.377	0.25040	Schmidt
Ar	He	0.273	0.24818	Lonius
		0.315	0.24965	Lonius
		0.677	0.25626	Lonius
		0.763	0.26312	Lonius

The conclusion reached from this program of experiments is that, while D varies with composition, in no case was the variation more than about 8 per cent of the mean value of D. The Stefan-Maxwell theory is therefore incomplete. The theory of interdiffusion, or transfer theory, gives the correct sense of the variation with composition but predicts a much greater amount of variation than is actually observed.

The transfer theory of diffusion is brought more nearly into accord with experiment through the theoretical work of Jeans[7] in applying a correction for persistence of velocities (see page 266). The researches of Chapman[5] and Enskog[6] on diffusion by more rigorous mathematical methods lead to formulæ which predict the actual variation of D with composition quite closely. As a result of these more advanced developments of the theory it may

be said that the experiments on this point are fully explained by the kinetic theory.

One more point remains on which comparison between theory and experiment may be made and that is as to the value of the factor ϵ, occurring in the equation

$$D = \epsilon \frac{\eta}{\rho},$$

in which D is the coefficient of diffusion of the gas into itself. Although this quantity cannot be determined experimentally, a method has been indicated by Lord Kelvin[13] whereby it may be estimated from data on the diffusivity of various pairs of gases. From the measurements of Loschmidt on diffusion and the modern data on viscosity the following table was compiled:

EXPERIMENTAL VALUES OF ϵ

Gas	D	ϵ (obs.)
H_2	1.31	1.37
O_2	0.189	1.40
CO	0.174	1.34
CO_2	0.109	1.50

It will be observed that all of these values lie between the extremes 1.200 for elastic spheres and 1.504 for molecules repelling according to the inverse-fifth-power law.

It must be added that the analyses of Chapman[5] and Enskog independently have led to the discovery of a new type of diffusion phenomenon. Maxwell's approach to the general study of transport phenomena was solved exactly by him for the case of molecules repelling as an inverse fifth power of the distance. In the extensions of this method to other laws of force, it turns out that for the general case when n in Gr^{-n} is greater than 5, there appear terms in the expression for diffusion which depend not only on $\partial N/\partial x$ but also on $\partial T/\partial x$ and $\partial p/\partial x$, where x is the direction of diffusion, and T and p are the temperature and pressure. Now, if T and p are not independent of x (*i.e.*, if T and/or p vary along the direction of diffusion), these terms take on values which are the greater as n becomes greater and of the same order of magnitude as the diffusion due to $\partial N/\partial x$.

Now it is possible to have a mixture of two gases in which $\partial N/\partial x$ is initially zero, but placed in a tube where there exist

pressure or temperature gradients. Experimentally pressure gradients make it impossible to proceed and are of little interest, but the effect of a temperature gradient can readily be studied. It turns out that because of the presence of the temperature gradient there will be a *diffusion* of *heavier* molecules to the lower temperatures. This diffusion process is called *thermal diffusion.* It will therefore produce a change in the composition of the mixture at the hot and cold ends of the tube which will increase until the ordinary diffusion just compensates the thermal process. The prediction of this phenomenon in 1917 by Chapman and Enskog independently, led Dootson[18] to set up a tube of an approximately equal mixture of CO_2 and H_2 (43.1 per cent H_2 and 56.9 per cent CO_2) with two bulbs at the ends kept at 230 and 10°C., respectively. After some hours, samples of the gas were drawn off at each end and analyzed. They showed in the hot bulb 44.9 per cent H_2 and 55.1 per cent CO_2, while in the cold bulb there were 41.3 per cent H_2 and 58.7 per cent CO_2. Thus the CO_2 had diffused into the colder bulb. Quantitatively the amount was not so great as would have been expected for elastic spherical molecules. The presence of the diffusion indicated, however, that the diffusion was present and that the molecules repelled with a force greater than Gr^{-5}. This phenomenon is most interesting as it is one that was discovered as a result of the generalized theory, and particularly so as it depends, not on forces, but on the *index of the law of force.* It is a very dramatic confirmation both of the method and of the assumptions concerning the repulsive forces.

References

1. See Reference 4, part II, of this chapter.
2. Tait, P. G.: "Scientific Papers," vol. 2, Sec. 78, p. 167 ff., Cambridge University Press, Cambridge; *Trans. Roy. Soc. Edinburgh*, p. 33, 1887.
3. Maxwell, J. C.: "Collected Scientific Papers," vol. 1, p. 392; vol. 2, pp. 57, 345.
4. Boltzmann, L.: *Sitzb. Akad. Wiss. Wien*, **64,** (II), 324, 1872; **78,** 783, 1878; **86,** 63, 1882; **88,** 835, 1883; as well as "Vorlesungen über die Gastheorie," vol. 1, p. 96, Johann Ambrosius Barth, Leipzig, 1910.
5. Chapman: *Phil. Trans. Roy. Soc.*, **217A,** 166, 1917.
6. Enskog: "Kinetische Theorie der Vorgänge in Mässig Verdünnten Gasen," Inaugural Dissertation, Upsala, 1917.
7. Jeans, J. H.: "Dynamical Theory of Gases," Chap. XIII. For full references see part II.
8. Loschmidt: *Sitzb. Akad. Wiss. Wien*, **61,** (II), 367, 468, 1870.

9. Byerly, W. E.: "Fourier's Series and Spherical Harmonics," Ginn & Company, Boston, 1893. (Dover Reprint)
10. Obermayer, V.: *Sitzb. Akad. Wiss. Wien*, **81** (II), 1113, 1880.
11. Stefan: *Sitzb. Akad. Wiss. Wien*, **63** (II), 63, 1871; and **65** (II), 323, 1872.
12. Lonius, A.: *Ann. Physik*, **29**, 664, 1909. Chapman, *Phil. Trans. Roy. Soc.*, **A211**, 478, 1911.
13. Kelvin: "Baltimore Lectures," p. 295.
14. Jeans, J. H.: "Dynamical Theory of Gases," 3d ed., Chap. XIII, p. 311.
15. Jeans, J. H.: *Loc. cit.*, p. 315.
16. Maxwell, J. C.: "Collected Works," vol. 2, p. 1.
17. Jeans, J. H.: *Loc. cit.*, p. 323.
18. Dootson, F. W.: *Phil. Mag.*, **33**, 248, 1917.

Books Recommended

a. Meyer, O. E.: "Kinetic Theory of Gases," translated by Baynes, Chaps. VII, VIII, IX; also Appendices IV, V, VI, Longmans, Green & Co., London, 1899.
b. Jeans, J. H.: *Loc. cit.*, Chaps. XI, XII, XIII. This book is excellent on this subject, giving excellent references with an admirable comparison of theory and experiment.
c. Jaeger, G.: Winkelmann's "Handbuch der Physik," Kinetische Theorie der Gase, vol. 3, pp. 734, 753; Johann Ambrosius Barth, Leipzig, 1906.

CHAPTER VII

THE LAWS OF RAREFIED GASES AND SURFACE PHENOMENA

76. Introduction.—The study of this phase of the subject may be begun from the historical point of view. The early investigations of gaseous viscosity were carried out largely by means of the study of the flow of gases in capillary tubes. It was shown from a theoretical deduction of the coefficient of viscosity η (Sec. 60) that the coefficient of viscosity is independent of the gaseous pressure through wide ranges of pressure. It fails to do this at low pressures, however, and the failure was ascribed to the fact that, as the pressure decreases, the mean free path becomes comparable with the dimensions of the apparatus used. Thus the assumptions made involving the statistical conditions under which η is defined no longer hold, and the flow cannot be treated in the usual way. The point at which the breakdown of this phenomenon occurs, however, depends on the dimensions of the apparatus used and the nature of the measurement. Its discussion, therefore, requires that the deviation be studied from the point of view of some given process of measurement. Historically, this occurred in a study of the laws of flow of gases through a capillary tube. At high pressures, and even down to a few millimeters of pressure the law of Poisseuille[1] holds. As the mean free path of the molecules approaches the diameter of the tubes used, the law fails. The failure is in the sense as if, instead of the velocity of flow being zero at the walls (an assumption made in deducing Poisseuille's law and which this law justified), it has a value greater than 0; that is, the gas appears to slip past the wall. The amount of gas coming out from a tube under these conditions therefore appears to be greater than the diameter of the tube would warrant. The experiments of Kundt and Warburg[2] in 1875 showed that an extension of the law of flow was necessary at low pressures, and indicated how this should be done. Theoretically, the conditions determining the flow were worked out successfully by Maxwell[3] for this case in

1879. The analysis of the failure of the law, however, remained incomplete until the measurements of Knudsen[4] in 1908 threw more light on it. It thus became possible to explain the phenomenon fairly completely. The further researches of Knudsen on this and other low-pressure phenomena following the work mentioned, directed attention to the possibilities of a successful treatment of such problems by kinetic-theory methods. It also led, together with the development of more powerful pumps, to a study of methods of low-pressure measurements. With the impetus given by these investigations, the theory of heat conduction in a gas at low pressures and the heat transfer from solid surfaces to gases at these pressures were carried on. Another phenomenon was also discovered and studied at low pressures. This is known as thermal transpiration. It consists of the flow of gas from a *cooler* rarefied body to a *hotter* one when these are connected by a capillary tube. In the development of the theory of heat conduction in a rarefied gas, together with the development of pressure-measuring devices, another set of phenomena received a study and some clarification. These are the so-called radiometric phenomena. The Crookes radiometer, so often seen in opticians' windows, consisting of a set of mica vanes blackened on one face and mounted on an axis so that they are free to rotate inside a partially evacuated glass vessel and which rotate when radiation falls on them, is a good example of this type of phenomena. The action of various types of instruments showing such effects have been quite recently studied from the standpoint of low-pressure conditions and have in some cases received a satisfactory explanation.

All these phenomena at low pressures in contradistinction to high-pressure phenomena emphasize the importance of impacts between molecules and the walls of the vessel relative to the intermolecular impacts so prominent at higher pressures. This has two effects: The first is to make the various phenomena observed much more a characteristic effect of the particular apparatus and experimental arrangement, thus making generalization partially impossible and conclusions drawn from observations apparently contradictory. The second effect is that it becomes necessary, to scrutinize, from the kinetic point of view, the nature of the momentum or energy exchange involved in collisions between gaseous molecules and solid surfaces. For instance, as will be seen in the discussion of capillary flow at low

pressures, the question arises as to whether the impinging molecules suffer specular reflection from the walls or whether they are reflected from the walls with a random distribution of velocities. Again, when molecules of one temperature strike a surface at another temperature one might well ask if the recoiling molecule left with the temperature of the surface or with a temperature intermediate between the two. This leads, therefore, to the study of the reflections of gas molecules from surfaces in general. The interpretations of the results of various observers lead to slightly differing answers to these questions, and at present there is no general completely satisfactory theory. It is possible that the different conditions actually lead to different processes of reflection, or, as stated above, the particular nature of the apparatus in each set of observations gives results so characteristic of the apparatus and conditions used that it is impossible to single out the true interpretation as regards the question of reflection.

Intimately connected with the question of reflection comes a question raised by the fact that a considerable proportion of the molecules appear to leave the solid surface with a random distribution of velocities. Overlooking the molecular roughness of the surfaces some observers are constrained to believe that the molecules actually condense on the solid surfaces and remain there for a period of time long compared to the time of a molecular gas impact. Thus the question of the formation of layers of gas molecules on surfaces, or perhaps, more generally, the question of "sorption" of gas molecules, is brought up. Outside of the possibility of the actual solution of the gas in the solid, true *absorption* (*e.g.*, the case of H_2 in Pd metal, or of H_2O in glass), two other types of surface absorption are shown to exist by Langmuir.[5] These are the *adsorbed* monomolecular layers of gas molecules, a *reversible* phenomenon (whose equilibrium is governed by temperature), and a chemical type of adsorption which depends on primary chemical valence forces. The latter type of adsorption is of great importance in phenomena of surface catalysis of chemical reactions.

In this chapter the subject of low-pressure phenomena will be introduced with a derivation of Poisseuille's law for capillary flow at high pressures, as this gives a clear and logical introduction to surface effects. The extension of this by Maxwell to low pressures will then be given, introducing Maxwell's assumptions. Then will follow Knudsen's contributions to the experimental

and theoretical sides of this question and a discussion of the effusion of gases at low pressures. Following this a section will be devoted to some of the questions of heat conduction at low pressures and the heat transfer to solid surfaces. In the succeeding section a summary of the question of molecular reflection from solid surfaces will be given together with a brief discussion of sorption, with special emphasis on Langmuir's work on adsorption. The theory of the molecular manometer of Knudsen and the problems of thermal transpiration will follow in the next sections. Following this there will be a brief discussion of repulsion radiometers, including the Crookes radiometer. It may be added that an excellent résumé of some of this work was written by Dunnoyer[6] in a small booklet of the series issued by the Société Française de Physique, Series 2, page 214, published by Gauthier-Villars, Paris, 1913.

77. Deduction of Poisseuille's Law of Flow of Gases through a Capillary Tube, and the Definition of the Coefficient of Slip.—

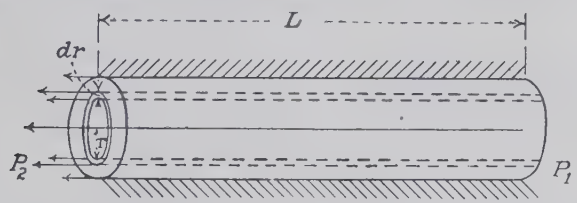

FIG. 44.

Assume a section of a capillary tube down which a gas is flowing as the result of a pressure difference $p_1 - p_2$ at its two ends. Take a small cylindrical section δr at a distance r from the axis of the tube (Fig. 44). The force F_1 acting on this is given by $2\pi r\delta r\text{-}(p_1 - p_2) = F_1$. If the flow has reached a steady state, equilibrium exists between this force and the forces of viscous drag acting across the boundaries of the surfaces, $2\pi rL$ and $2\pi(r + \delta r)L$ of the section, where L is its length. The force F_2 on these surfaces is composed of two components. The first component F_{2i} is that of the inner faster layer of gas and is given by an equation of the form $F = \eta S\frac{dv}{dr}$ by the definition of viscous drag, where S is the area of the cylindrical surface, η the coefficient of viscosity, and $\frac{dv}{dr}$ is the velocity gradient. As $\frac{dv}{dr}$ is negative, for v decreases as r increases, and as $S = 2\pi rL$, $F_{2i} =$

$-2\pi\eta r L\frac{dv}{dr}$. The second component F_{2o} is the drag produced by the slower outer layer of gas of surface $S = 2\pi(r + dr)L$. As here the gradient of velocity is $-\frac{d\left(v + \frac{dv}{dr}\delta r\right)}{dr}$, the force F_{2o} is $F_{2o} = -2\pi\eta(r + \delta r)L\frac{d\left(v + \frac{dv}{dr}\delta r\right)}{dr}$. Now $F_2 = F_{2o} - F_{2i}$, and for equilibrium $F_1 = F_2 = F_{2o} - F_{2i}$. One therefore has for the differential equation of flow

$$2\pi r(p_1 - p_2)\delta r = -2\pi\eta(r + \delta r)L\frac{d\left(v + \frac{dv}{dr}\delta r\right)}{dr} + 2\pi\eta r L\frac{dv}{dr}.$$

Canceling common terms and reducing the equations,

$$(p_1 - p_2)r = -\eta L\left(r\frac{d^2v}{dr^2} + \frac{dv}{dr}\right)$$

if one neglect the term $-\eta L\frac{d^2v}{dr^2}\delta r^2$, which is an infinitesimal of the second order. Hence

$$-\frac{p_1 - p_2}{\eta L} = \frac{d^2v}{dr^2} + \frac{1}{r}\frac{dv}{dr}.$$

Since $\frac{p_1 - p_2}{\eta L}$ is a constant of the apparatus, $\frac{d^2v}{dr^2}$ and $\frac{1}{r}\frac{dv}{dr}$ are both constant. A particular solution* of such an equation will take the form $v = A + Br^2$, where A and B are constants to be determined. Now

$$\frac{dv}{dr} = 2Br \qquad \frac{1}{r}\frac{dv}{dr} = 2B$$
$$\frac{d^2v}{dr^2} = 2B, \text{ thus } 4B = -\frac{p_1 - p_2}{\eta L},$$

whence

$$v = A - \frac{p_1 - p_2}{4\eta L}r^2.$$

* The solution of the differential equation above can, of course, be undertaken by more general methods. The general solution does not differ from the one above except for the presence of an exponential term which vanishes when the boundary conditions are fulfilled. The method of solution outlined above is simpler than the rigorous solution and so is given at this point.

If $v = 0$ when $r = R$, where R is the radius of the tube, *there is no slip* at the surface of the tube and the equation yields $0 = A - \frac{p_1 - p_2}{4\eta L}R^2$, whence $A = \frac{p_1 - p_2}{4\eta L}R^2$.

Thus the layer δr at a distance r from the axis of the tube has a velocity v given by

$$v = \frac{(p_1 - p_2)}{4\eta L}(R^2 - r^2).$$

To get the volume V of gas flowing out of the tube per second it is necessary to integrate $v(2\pi r dr)$, the volume flowing out of a layer dr from $r = 0$ to $r = R$, the radius of the tube.

$$V = \int_0^R 2\pi r \frac{(p_1 - p_2)}{4\eta L}(R^2 - r^2)dr$$
$$= \frac{\pi(p_1 - p_2)R^4}{8\eta L}.$$

If L is short, a correction should be made for the turbulent flow at the orifices. For sufficiently long tubes the law holds well, the length necessary for this depending on the value of R. Again, as was stated in the preceding section, when the pressures are low or when $p_1 - p_2$ is very great the law fails, for then v is not 0 when $r = R$. That is, the gas slips past the walls with a velocity v_0 at the walls.

To take care of slip at the walls it must be remembered that the assumption that $v = 0$ when $r = R$ was made in order to determine A. In order to handle the case when $v = v_0$ at $r = R$ it becomes necessary to assume that at $r = R$ there is a frictional force f on the surface of the gas at the tube wall. This force f may be written $f = \epsilon S v_0$; where $S = 2\pi RL$, v_0 is the velocity of the gas at $r = R$, and ϵ is a numerical coefficient of the force. The force at the boundary due to its drag is therefore proportional to the velocity and the surface, while its magnitude is controlled by these and a numerical coefficient of considerable theoretical interest. With these assumptions the condition for equilibrium at the wall (*i.e.*, when $r = R$) will be given by the following equation:

$$2\pi R\delta r(p_1 - p_2) = f - \left(-2\pi RL\eta\frac{dv}{dr}\right),$$

where the first term is the force F_1 due to the pressure on the layer δr at $r = R$, f is F_{2v}, which is now the drag due to the walls,

and $-2\pi RL\eta \frac{dv}{dr}$ is F_{2i}, the drag of the inner gas on the gas at the surface. If the layer δr be taken sufficiently small, the term $2\pi R\delta r(p_1 - p_2)$ becomes 0. Thus

$$-2\pi R\eta L \frac{dv}{dr} = f = 2\pi RL\epsilon v_0, \text{ or } v_0 = -\frac{\eta}{\epsilon}\frac{dv}{dr}.$$

But in the preceding analysis

$$\frac{dv}{dr} = -\frac{1}{2}\frac{p_1 - p_2}{\eta L} r,$$

whence

$$v_0 = \frac{r}{\epsilon}\frac{p_1 - p_2}{2L}.$$

With this expression for $v = v_0 = \frac{r}{\epsilon}\frac{p_1 - p_2}{2L}$ at $r = R$, one may determine A by

$$v_0 = A - \frac{p_1 - p_2}{4\eta L}R^2 = \frac{R}{\epsilon}\frac{(p_1 - p_2)}{2L},$$

or

$$A = \frac{(p_1 - p_2)}{4\eta L}\left(R^2 + \frac{2R\eta}{\epsilon}\right).$$

This yields for v, the velocity at r, the expression

$$v = \frac{(p_1 - p_2)}{4\eta L}\left(R^2 - r^2 + 2R\frac{\eta}{\epsilon}\right),$$

and for the volume of gas flowing out per second the expression

$$V = \frac{\pi(p_1 - p_2)}{8\eta L}\left(R^4 + \frac{4\eta}{\epsilon}R^3\right).$$

Here ϵ is a constant of the walls and the gas. This equation shows that when measurements are made roughly the slip at the walls may be neglected. The deviation from the first equation deduced may be seen at once from

$$V = \frac{\pi(p_1 - p_2)}{8\eta L}R^4\left(1 + \frac{4\eta}{\epsilon R}\right).$$

It depends on R. If R is large compared to $\frac{4\eta}{\epsilon}$, it can be neglected.

The ratio $\frac{\eta}{\epsilon}$ which determines the question of the importance of this term in the theory is called the "coefficient of slip" and is

designated symbolically by $\zeta = \frac{\eta}{\epsilon}$. It really gives the ratio of the internal friction of the gas (*i.e.*, the coefficient of the viscosity) to the coefficient of external friction against the walls. The value of ϵ, and consequently of ζ, must depend on the nature of the impacts which are assumed between the gas and the walls. It is therefore necessary to derive an expression for this quantity in terms of the kinetic theory before proceeding further. The relation to be considered is due to Maxwell and its detailed consideration cannot find place here. The ideas used, however, will be developed at this point, together with the result.

If the surface were perfectly smooth, specular or perfect reflection would be observed, that is, the molecules striking the surface at any angle ϕ (Fig. 45) would rebound, conserving the velocity

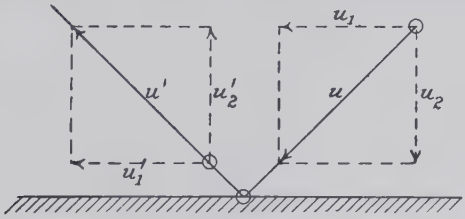

FIG. 45.

parallel to the surface, but having the component of velocity perpendicular to the surface reversed. With such reflection the only force on the wall would be the pressure normal to it. The velocity at the surface would then be the velocity of flow along the wall (*i.e.*, there would be no drag, ϵ would be 0, and the gas would flow down the tube with no action on the walls), that is, its velocity through the cross-section of the tube would be uniform. This is not the case, for actually there is a frictional term. This means that there must be some mechanism by which the gas is retarded by the walls. If the walls were composed of spherical gas molecules at rest with large spaces between them, the molecules striking such a wall would lose their momentum, for, on the average, they would be reflected as if they had velocities after reflection equally probable in all directions. Maxwell points out that such molecules could be considered as "*absorbed and reevaporated*" from the surface at a temperature corresponding to that of the gas, if the wall and the gas are at the same temperature. With such a process occurring, the gas would still have a velocity of slip. In this case, however, the velocity at the wall

would be less than that in the center and the gradient could be calculated. How this occurs can easily be seen. The molecules leaving the surface must equal those approaching it when equilibrium has set in. Those leaving have random velocities, and hence no streaming velocity down the tube. Those approaching the walls have an average velocity component v appropriate to the scenes of their last impacts in the gas. Thus the layer of gas nearest the wall is composed, on the average, of equal numbers of molecules with zero streaming velocity and with an average velocity v. There will thus be a velocity jump at the surface equivalent to $\frac{v}{2}$. If the molecules of the wall are not distributed as assumed by Maxwell, they may partly specularly reflect the impinging molecules. In such a case the slip will be greater than that above, and v_0 will be increased. Actually, the surface molecules of the solid are not necessarily distributed to give diffuse reflection, but, as Maxwell points out, they act so as to shield each other from direct impacts of gas molecules. The result will be that very oblique impacts will cause reflection from the outer ends of the wall molecules. They will thus be more nearly specularly reflected than will the molecules striking normally. The outcome of this will be that there will be a slip in the gas which will depend on the relative importance of the two kinds of reflection. To study this, he assumes that those molecules striking a fraction f of the surface will be absorbed, and $1 - f$ will be specularly reflected. To calculate the slip he then proceeds as follows: Assume the gas to be flowing along y past a plane surface yz, and that the positive x direction is the direction of the gas from the wall. Call u, v, and w the components of velocity along the three axes. If, now, a particular velocity be chosen one may term $-u_1$ the incident value of the x component, and $+u_2$ as the rebounding value of the x component of the molecules that are specularly reflected. The x component of the evaporated molecules will be $+u'$. The mass of gas of velocity component $-u_1$ incident on unit surface of the plane per unit time is, then, $-\rho_1 u_1$, where ρ_1 is the density of molecules of velocity component u_1 in the gas. Of these molecules the fraction $1 - f$ has u reversed in direction. For the fraction f evaporated, the average component of velocity is u', corresponding to the temperature Θ' of the wall. With these considerations one may write that for the fraction f that are absorbed the

momentum normal to the surface must equal the momentum of the same molecules reevaporated from the surface at the same temperature, that is,

$$-f\rho_1 u_1 = f\rho_2' u_2'.$$

It also follows that the total momentum given to the wall by the molecules leaving is expressed by

$$\rho_2 u_2 = -(1-f)\rho_1 u_1 + f\rho_2' u_2',$$

where ρ_1, ρ_2, and ρ_2' are the densities of the molecules having velocities u_1, u_2, and u_2'.

Along the direction of motion y the velocity is v, and the incident momentum is $\rho_1 u_1 v$, the mass striking per unit time times the incident velocity v. Of these, $1-f$ are specularly reflected and $(1-f)\rho_1 u_1 v_1$ is the momentum along the wall which is not changed, that is, this is the momentum exchange which causes the additional slip. The momentum of the evaporated portion along y which has an average velocity component $-v$ (the relative velocity between gas and the surface) is, then, $-f\rho_2' u_2' v$. The expression for the momentum of the reflected molecules along y is, then, expressed by the relation

$$\rho_2 u_2 v_2 = (f-1)\rho_1 u_1 v_1 - f\rho_2' u_2' v.$$

Between this and the preceding equations the quantities $f\rho_2' u_2'$ can be eliminated and one has for the momentum transfer the following equation:

$$(1-f)\rho_1 u_1 v_1 + \rho_2 u_2 v_2 + v[(1-f)\rho_1 u_1 + \rho_2 u_2] = 0.$$

To solve this in order to get the velocity of the gas along the wall, the appropriate values for ρ_1, ρ_2, u_1, u_2, v_1, v_2, and v must be put into the equation, and integrated for u from $-\infty$ to 0 and with respect to v and w from $-\infty$ to $+\infty$, and for the molecules which are leaving the surface for u from 0 to ∞. The functions to be inserted are taken from a more general expression deduced by Maxwell for the case where the temperatures of the wall and gas may be different. They are too lengthy to include in this place. With certain simplifications to facilitate solution and the assumption that the temperatures of the gas and the wall are the same, he finds that the velocity of the gas at the wall is given by

$$v_0 = \sqrt{\frac{\pi}{2}}\eta\sqrt{\frac{1}{p\rho}}\left(\frac{2-f}{f}\right)\frac{dv}{dx},$$

where $\frac{dv}{dx}$ is the gradient of velocity normal to the wall. It is seen that when $f = 1$, $v_0 = \sqrt{\frac{\pi}{2}}\,\eta\sqrt{\frac{1}{p\rho}}\,\frac{dv}{dx}$, a minimum value, and as f decreases v_0 rapidly increases. For the case of the flow in a tube $\frac{dv}{dx}$ is replaced by the $\frac{dv}{dr}$ above, and one has

$$v_0 = \frac{\eta}{p}\sqrt{\frac{\pi}{2}\frac{R_0T}{M}}\left(\frac{2-f}{f}\right)\frac{dv}{dr},$$

where M is the mass of a gram-molecule, R_0 is the gas constant per gram molecule, and T is the absolute temperature. But it was found in deducing the slip term of Poisseuille's equation that

$$v_0 = +\frac{\eta}{\epsilon}\frac{dv}{dr} = \zeta\frac{dv}{dr},$$

whence

$$\zeta = \frac{\eta}{\epsilon} = \frac{\eta}{p}\sqrt{\frac{\pi}{2}\frac{R_0T}{M}}\left(\frac{2-f}{f}\right).$$

This at once gives the value of the coefficient of slip ζ in terms of the fraction f of the molecules evaporated from the surface, or the fraction $1 - f$ specularly reflected. It is thus seen that the term $\zeta = \frac{\eta}{\epsilon}$ in Poisseuille's law depends on the $\sqrt{T}$, on f, and on $\frac{1}{p}$. It is the variation of $\frac{\eta}{\epsilon}$ with pressure that is of interest, for the correction term for slip in Poisseuille's law depends on $\left(1 + \frac{4\eta}{\epsilon R}\right)$. As long as pR is large compared with the other quantities, the term may be neglected, but when p becomes small the correction must be added. One is now in a position to compare the theory with experiment.

Before doing this it might be stated that Baule[7] also found an expression for the coefficient of slip similar to that of Maxwell to a first approximation. Baule interprets f in terms of a coefficient which gives the fraction of molecules which make only one impact with the walls of the solid. Thus such molecules do not come into complete equilibrium with the walls, and retain some of their incident velocity. Those that escape after several impacts have the random distribution of the evaporated molecules of Maxwell. If $f = 1$, his formula becomes identical with Maxwell's. It

merely makes a more accurately analytical picture of what takes place at the wall. A very accurate measurement of the coefficient of slip was made by Blankenstein.[8] He used the rotating-cylinder method (see Sec. 63) in the gases H_2, He, air, and O_2 where the gases were kept very pure by a constant-flow method at low pressures. The surfaces were burnished surfaces of silver oxide deposited on brass. In this method the deflection is related to the momentum transfer of the gas by the factor $\eta\left(\frac{V}{d}\right)$ at high pressures. Here $\frac{V}{d}$ is the velocity gradient at the surface, d being the separation of the cylinders and V the velocity of the moving cylinder. If slip appears, the momentum transfer is lessened and it may be written as $\frac{\eta V}{(d + 2\zeta)}$, where ζ is the coefficient of slip defined above. By measuring the deflection of the cylinder at higher pressures and again at pressures where slip occurs, it should be less at the low pressures in the ratio $\frac{d}{(d + 2\zeta)}$. By measuring this difference at different low pressures, ζ may be computed as a function of p. From the values of ζ and p it is possible to determine f. For the gases He, H_2, air, and O_2 the values of f obtained were 1.00, 1.00, 0.98, and 0.99 respectively. Thus it might be concluded that there is practically no specular reflection for H_2 and He, while air and O_2 show about 1 or 2 per cent of slip. Other experiments by Van Dyke[9] and Stacy,[10] using shellac and oil surfaces with gases of a more doubtful purity, gave a specular reflection of from 8 to 20 per cent. The question of such reflection will, however, be more properly treated later on. The verification of Maxwell's equation, no matter what the theoretical basis of f, places this mode of procedure as a legitimate one. It is thus permissible to consider the apparent change in the outflow from a tube as pressure decreases, found by Kundt and Warburg,[2] from this point of view. The equation for the volume of gas flowing out of a tube as a function of the various quantities entering in was given as

$$V = \frac{\pi(p_1 - p_2)}{8\eta L} R^4\left(1 + \frac{4\eta}{\epsilon R}\right).$$

This can be changed to the mass of gas G flowing out in unit time, which is what is actually measured. As $p = \frac{1}{3}\rho C^2$, where ρ is the

density, and as $\frac{1}{3}mN_AC^2 = \frac{1}{3}MC^2 = R_0T$, where M is the mass of a gram-molecule, therefore $\rho = \frac{pM}{R_0T}$. Since $G = V\rho$, the equation for G becomes

$$G = \frac{\pi R^4}{8\eta L}(p_1 - p_2)\frac{M}{R_0T}p\left(1 + 4\zeta\frac{1}{R}\right).$$

Thus G plotted as ordinates against p as abscissæ is a straight line that should pass through the origin. As the pressure becomes very low, the factor $\left(1 + \frac{4\zeta}{R}\right)$ becomes appreciable, for ζ is proportional to $\frac{1}{p}$, as shown by Maxwell's theory. This causes G to decrease more slowly as p decreases, for the ζ which increases as p decreases counteracts the effect of pressure in decreasing G. This portion of the curve was that studied by Kundt and Warburg and it is explained by slip.

As the pressures decrease still more, the flow at first rises as pressure decreases and finally ceases to change with pressure at all, remaining constant. It was the portion of the curve for G, just before the rise and from there on, for which the theory was incomplete and was extended by the work of Knudsen[11] in 1909.

78. Flow in Tubes for Rarefied Gases, Knudsen's Equation.—The constant régime sets in when the pressures are so low that the mean free path of the gas molecules is comparable with R. If this occurs one cannot speak of a flow in the ordinary sense at all. It is perhaps best to discuss and interpret the régime of constant outflow first, for the transition from the Kundt and Warburg deviation from the straight line to the constant outflow through the minimum marks a transition from one type of mechanism of flow to the other which cannot be clearly grasped until the initial and final conditions of flow are understood.

The derivation of the equation for this régime, due initially to Knudsen, is very instructive. He starts with the assumption that the number of molecules striking a cm^2 of surface per second is $\frac{1}{4}N\bar{c}$ (see Secs. 40 and 71), where $\bar{c}$ is the average velocity of the molecules. If there are N molecules per cm^3, the number dN with velocity components between c and $c + dc$ is given by the Maxwell distribution law as

$$dN = \frac{4N}{\alpha^3\sqrt{\pi}}c^2e^{-\frac{c^2}{\alpha^2}}dc,$$

where α is the most probable speed. The number of these molecules which strike 1 cm^2 of surface per second is, then, $\frac{1}{4}cdN$. Since the molecules which have a component of velocity of translation ω parallel to the wall on striking are absorbed, and reemitted equally in all directions (that is, with the f of Maxwell equal to 1), the momentum given the wall by these dN molecules is $\frac{1}{4}cm\omega dN$. Since ω is the component of the velocity of the gas molecules parallel to the wall, ω may be written kc where k is a constant of proportionality. This merely expresses ω as a fractional part of c, the molecular velocity, and ascribes the Maxwell distribution to the components ω in this manner. The momentum transfer is, therefore, $\frac{1}{4}kc^2mdN$. The momentum B given the wall by molecules of all velocities is therefore given by

$$B = \frac{1}{4}Nk\frac{4}{\sqrt{\pi}}m\int_0^\infty \frac{c^4}{\alpha^3}e^{-\frac{c^2}{\alpha^2}}dc = \frac{1}{4}Nkm\frac{3}{2}\alpha^2.$$

Substituting $\bar{c}$ for α, where $\bar{c} = \frac{2\alpha}{\sqrt{\pi}}$, one gets $B = \frac{3\pi}{32}Nmk\bar{c}^2$.

As $\bar{c}$ is $\frac{\Sigma c}{N}$, therefore $k\bar{c} = \frac{\Sigma kc}{N} = \frac{\Sigma\omega}{N} = v$.

This v is the geometric mean of the velocity of all molecules. It is therefore the velocity of the mass of gas down the tube, and one has $B = \frac{3\pi}{32}Nm\bar{c}v$. This assumes v constant across the tube. This assumption only holds, in the Knudsen régime, where the free path is great compared to the radius of the tube, and hence there is no velocity gradient normal to the walls. Physically, this means that the gas is so rarefied that the velocity transition at the surface which was confined to a narrow region originally now extends across the whole tube.

For a tube of approximately cylindrical form, call dl the element of length of the tube, O its circumference at dl, and A its area of cross-section. In dt sec. this tube receives an amount of momentum given by $\frac{3\pi}{32}Nm\bar{c}vOdldt$. Setting $Nm = \rho$, the density of the gas, and expressing $\bar{c}$ in terms of the pressure p,

from the relation $p = \frac{\pi}{8} N m \bar{c}^2$, the above quantity becomes

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\sqrt{\frac{p}{\rho}}\,v O dl dt.$$

If it is assumed that the wall Odl gets the whole momentum which results from the pressure drop $-\left(\frac{dp}{dl}\right)dl$ (that is, neglecting the end effects of the tube), one obtains the relation between the momentum transfer $-A\left(\frac{dp}{dl}\right)dldt$ in the time dt due to the pressure difference across the area A, and the momentum transfer to the wall as

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\sqrt{\frac{p}{\rho}}\,vO = -A\frac{dp}{dl}.$$

For the mass G which goes through the area per second one can write $G = A\rho v$, whence

$$G = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\sqrt{\frac{\rho}{p}}\,\frac{A^2}{O}\frac{dp}{dl}.$$

If the ratio of the density and pressure, when the pressure is in dynes per cm^2, is called ρ_1; then

$$G = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\sqrt{\rho_1}\,\frac{A^2}{O}\frac{dp}{dl}.$$

If the volume of gas per unit pressure flowing through the tube be used instead of the mass of the gas, that is, if one write $Q_t = \frac{G}{\rho_1}$, then

$$Q_t = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\,\frac{1}{\sqrt{\rho_1}}\,\frac{A^2}{O}\frac{dp}{dl}.$$

For steady flow, Q_t has the same value along the tube. Calling the length of the tube L and the pressure on its ends p_1 and p_2, $(p_1 > p_2)$, one obtains

$$Q_t\frac{O}{A^2}dl = -\frac{8}{3}\sqrt{\frac{2}{\pi}}\frac{1}{\sqrt{\rho_1}}dp,$$

which yields on integration

$$Q_t = \frac{1}{\sqrt{\rho_1}}\,\frac{(p_1 - p_2)}{\frac{3}{8}\sqrt{\frac{\pi}{2}}\int_0^L \frac{O}{A^2}dl} = \frac{1}{\sqrt{\rho_1}}\,\frac{p_1 - p_2}{W},$$

that is,

$$Q_t = \frac{p_1 - p_2}{\sqrt{\rho_1} W},$$

where

$$W = \frac{3}{8}\sqrt{\frac{\pi}{2}} \int_0^L \frac{O}{A^2} dl.$$

W is a constant of the form and dimensions of the tube only. It has the same function as a resistance factor in electricity, and can be called the resistance of the tubes. Thus it is possible for this case of flow in tubes to carry over Kirchhoff's laws of branched circuits to the calculation of the gaseous flow in any system of tubes. For a cylindrical tube of radius R, $O = 2\pi R$ and $A = \pi R^2$, whence

$$W = \frac{3}{8}\sqrt{\frac{\pi}{2}} \frac{2}{\pi} \frac{L}{R^3},$$

and

$$Q_t = \frac{4}{3}\sqrt{2\pi} \frac{1}{\sqrt{\rho_1}} \frac{R^3}{L} (p_1 - p_2).$$

Where gases flow out of the ends of the tubes with a finite velocity, the whole pressure drop is not taken up in overcoming wall resistance, for the gas has a kinetic energy on leaving the tube which it got from the pressure difference. In this case the relation

$$\frac{3}{8}\sqrt{\frac{\pi}{2}} \rho \sqrt{\frac{p}{\rho}}\, vO = -A\frac{dp}{dl},$$

must be replaced by

$$\frac{3}{8}\sqrt{\frac{\pi}{2}} \rho \sqrt{\frac{p}{\rho}}\, vO = -A\frac{dp}{dl} - A\rho v\frac{dv}{dl},$$

where $G = A\rho v$ is the mass of the gas flowing out per second, and $\frac{dv}{dl}$ is the change in velocity per unit length of tube. Thus

$$\frac{3}{8}\sqrt{\frac{\pi}{2}} \frac{1}{\sqrt{\rho_1}} \frac{O}{A^2} G = -\frac{dp}{dl} - \frac{G^2}{A^2\rho_1} \frac{d}{dl}\left(\frac{1}{\rho}\right),$$

which on integration over the whole tube yields

$$\frac{3}{8}\sqrt{\frac{\pi}{2}} \frac{1}{\sqrt{\rho_1}} G \int_0^L \frac{O}{A^2}\, dl = p_1 - p_2 - \frac{G^2}{A^2\rho_1} \frac{p_1 - p_2}{p_1 p_2}.$$

Again setting

$$W = \frac{3}{8}\sqrt{\frac{\pi}{2}} \int_0^L \frac{O}{A^2}\, dl,$$

then

$$G = (p_1 - p_2)\frac{\sqrt{\rho_1}}{W}\frac{1}{1 + \dfrac{G}{A^2\sqrt{\rho_1}W}\dfrac{p_1 - p_2}{p_1 p_2}}.$$

If the quantity

$$U = \frac{G}{A^2\sqrt{\rho_1}W}\frac{p_1 - p_2}{p_1 p_2}$$

is small compared to 1, one obtains the previous relation $G = \frac{\sqrt{\rho_1}}{W}(p_1 - p_2)$ and the quantity U becomes

$$U = \frac{1}{A^2 W^2}\frac{(p_1 - p_2)^2}{p_1 p_2}.$$

For a cylindrical tube this is

$$U = \frac{32}{9\pi}\frac{R^2}{L^2}\frac{(p_1 - p_2)^2}{p_1 p_2}.$$

As U depends on $\frac{R}{L}$, it is seen that, for experimental cases where $\frac{R}{L}$ is of the order of $1/100$, U must be much less than unity, even when p_1 is hundreds of times greater than p_2.

Thus the mass discharged per sec from a cylindrical tube at low pressures can be taken as

$$G = \frac{4}{3}\sqrt{2\pi}\sqrt{\rho_1}\frac{R^3}{L}(p_1 - p_2).$$

This differs materially from the Poisseuille's equation, having a coefficient of slip which reads

$$G = \frac{\pi R^4}{8\eta L}(p_1 - p_2)\frac{M}{R_0 T}\left(1 + \frac{4\eta}{\epsilon}\frac{1}{R}\right)p.$$

The comparison is clearer if, for ρ_1, the quantity $\frac{\rho}{p}$ is used, for then

$$\frac{Nm}{\frac{1}{3}NmC^2} = \frac{\rho}{p} = \frac{N_A m}{R_0 T} = \frac{M}{R_0 T},$$

whence

$$G = \frac{4}{3}\sqrt{2\pi}\sqrt{\frac{M}{R_0 T}}\frac{R^3}{L}(p_1 - p_2).$$

It is seen that for low pressures G is proportional to R^3, and not R^4 as in Poisseuille's law. Furthermore, G is independent of η and p.

The discussion of the minimum of the curves presupposes a comparison with the experimental results. In Figs. 46, 47*a*, and

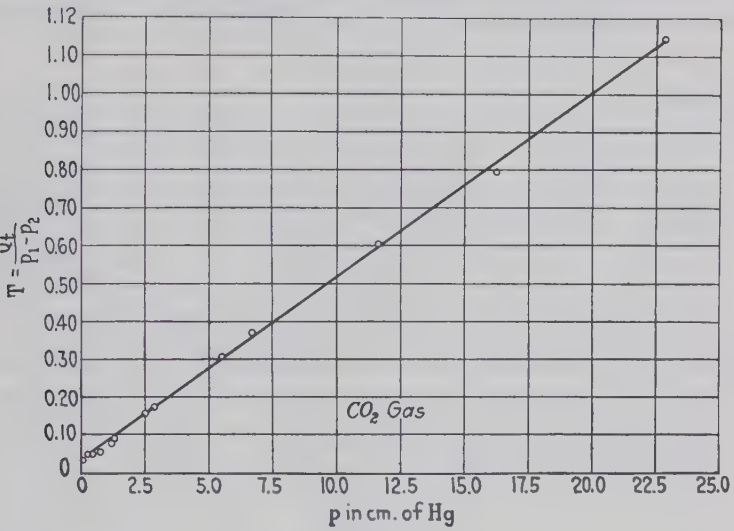

FIG. 46.

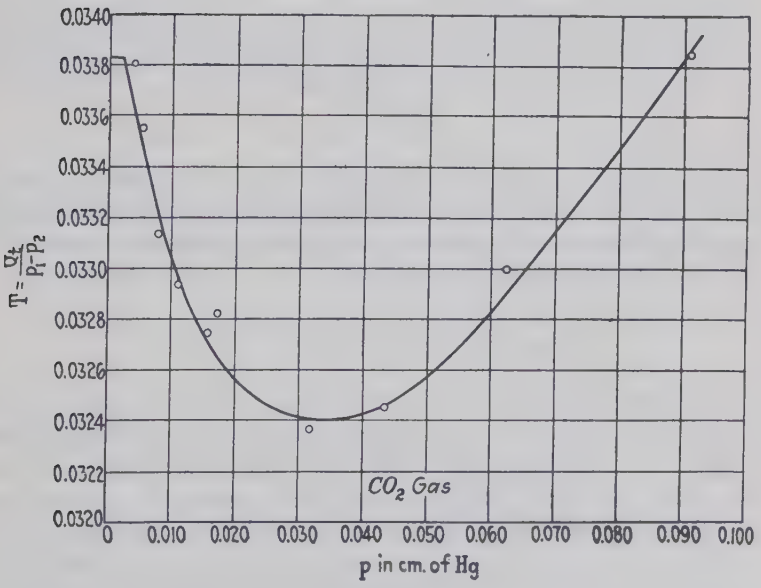

FIG. 47*a*.

47*b* the points found by Knudsen in CO_2 for a certain tube are given. In them $T = \dfrac{Q_t{}^*}{p_1 - p_2}$ is plotted against p in cm of mer-

* $Q_t = \dfrac{G}{\rho_1} = \dfrac{GM}{R_0 T}$.

cury. The régime from $p = 0.004$ cm to $p = 0.000011$ cm is shown in Fig. 47*b* on a logarithmic scale. As is seen at once, T decreases linearly with p from 22 to about 0.24 cm. From then

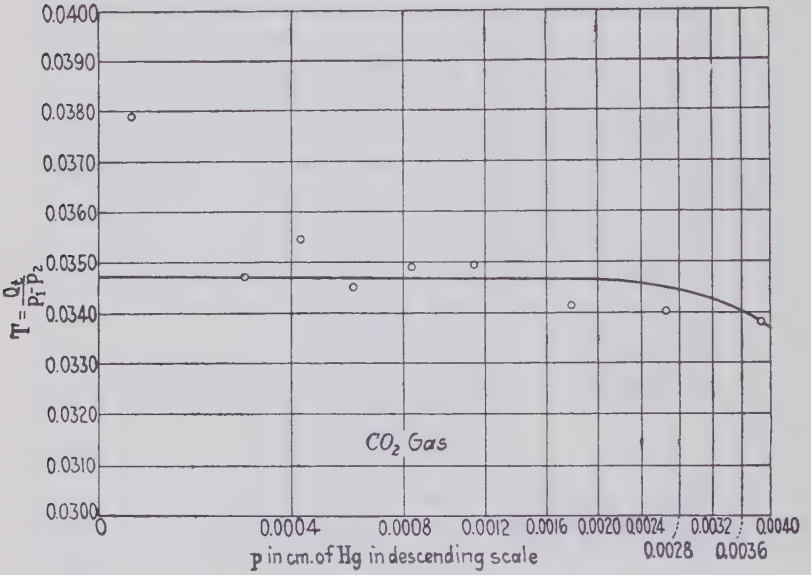

FIG. 47*b*.

on it falls to a minimum, rising again to $p = 0.0010$ cm, from which point on it remains as constant as the measurements will permit. The smooth curves which fit the results quite accurately are given by an empirical expression

$$T = ap + b\frac{1 + c_1 p}{1 + c_2 p},$$

where the constants a, b, c_1, and c_2 can be found from least-square reductions. These constants depend on the dimensions of the tube and other factors. All tubes used gave similar curves, the constants only differing. It is first necessary to correlate as many of the constants as possible with the constants deduced thus far from the theory. This is easily done for the constants a and b. The constants c_1 and c_2, however, are the ones related to the minimum of the curve. And it is their evaluation which will throw light on this process.

The constant a can be evaluated as follows. If Poisseuille's law is assumed to hold with no slip at the walls, it yields

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p.$$

This term is equivalent to the portion $T = ap$ of the empirical equation. The a should then be given by $a = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}$. Calculating a for his tubes from this expression, Knudsen finds agreement with the observed values within the limits of experimental uncertainty.

For small values of p the equation goes over to the form $T = b$, for ap and $\frac{1 + c_1 p}{1 + c_2 p}$ become 0 and 1 respectively in this case. For the lowest pressures one has the conditions of molecular flow, in which $T = \frac{1}{W\sqrt{\rho_1}}$, and for cylindrical tubes of circular cross-section $T = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}$. Hence b becomes $b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}$.

To obtain the values of c_1 and c_2, two cases must be considered. The first one is for pressures where the free path is small compared to the radius of the tube, but not negligibly small. The study of this case will give a ratio of the constants $\frac{c_1}{c_2}$ The second one is where the radius of the tube is smaller than the mean free path, but is not vanishingly small compared to this. The study of this condition leads to an evaluation of $c_2 - c_1$. The two cases together then afford means of obtaining c_1 and c_2.

For the first case p is so great that $\frac{1 + c_1 p}{1 + c_2 p}$ may be written as $\frac{c_1}{c_2}$. The equation then becomes $T = ap + b\frac{c_1}{c_2}$. Putting in the values of a and b one has that

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p\left(1 + \frac{32\sqrt{2}\,\eta}{3\sqrt{\pi}\sqrt{\rho_1}\,Rp}\frac{c_1}{c_2}\right).$$

But in this régime (which is that of Kundt and Warburg) Poisseuille's equation also holds, including the slip term. This law gives $T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p\left(1 + \frac{4\zeta}{R}\right)$. Comparing the two expressions

for T, one has at once that $\zeta = \dfrac{8\sqrt{2}\eta c_1}{3\sqrt{\pi}\sqrt{\rho_1}pc_2}$. The expression $\zeta = \dfrac{\eta}{\epsilon} = \dfrac{\eta}{p}\sqrt{\dfrac{\pi}{2}}\dfrac{R_0T}{M}\left(\dfrac{2-f}{f}\right) \equiv k\lambda$ is similar to the mean free path, so that ζ can be replaced by $k\lambda$, where k is a fraction nearly equal to 1 and λ is the mean free path. Also, since Maxwell's distribution law gives a relation between λ and η of the form

$$\lambda = \frac{\sqrt{\dfrac{\pi}{8}}}{0.30967}\frac{\eta}{p\sqrt{\rho_1}},$$

then

$$\frac{k\sqrt{\pi}\eta}{\sqrt{8}(0.30967)\,p\,\sqrt{\rho_1}} = \frac{8\sqrt{2}\eta c_1}{3\sqrt{\pi}\sqrt{\rho_1}pc_2},$$

that is, $\dfrac{c_1}{c_2} = 0.95k$. As k is less than unity, $\dfrac{c_1}{c_2}$ is a constant independent of the radius of the tube and the nature of the gas whose value is less than 0.95. In fact, Knudsen's experiments bear out the fact that $\dfrac{c_1}{c_2}$ is between 0.85 and 0.78 and is independent of tube radius, specific gravity, or viscosity of the gas, and he chooses $\dfrac{c_1}{c_2} = 0.81$.

The evaluation of $c_2 - c_1$ is a far more complicated question, for which there is not room in this text. The general considerations by which this end is reached are instructive, and may therefore briefly be indicated. At pressures where the free path is greater than the dimensions of the tube, but not much greater, both impacts with the walls and with other molecules occur. The momentum of the moving molecules can then be carried to the walls by two processes: either by direct impact with the walls, or by the molecules struck by these molecules, which therefore have some of the streaming motion. The former can be computed from the number of molecules striking unit area of the walls, which is $\dfrac{N\bar{c}}{4}$. The momentum carried by these two mechanisms can then be roughly evaluated. Allowance must be made in this calculation for the time elapsing between the impacts of the moving molecules and the others, and the transfer of this momentum to the walls. This calculation leads to the use of a

small numerical factor k of a value about ½. The use of k yields for a cylindrical tube of circular cross section the value

$$T = \frac{4}{3}\sqrt{2\pi}\,\frac{1}{\sqrt{\rho_1}}\,\frac{R^3}{L}\left(1 - (1-k)\,\frac{2R}{\lambda}\right).$$

Comparison with the empirical equation, which for the approximate values of p for which this occurs takes on the form

$$T = ap + b[1 - (c_2 - c_1)\,p]$$

leads to the relation

$$(1-k)\,\frac{2R}{\lambda} = \left(c_2 - c_1 - \frac{a}{b}\right)p.$$

Inserting the expression for λ on the preceding page the equation, on rearrangement, becomes

$$c_2 - c_1 = 1.2378\,\frac{R}{p\lambda} = 0.6117\,\frac{\sqrt{\rho_1}}{\eta}R$$

in the event that $k = ½$, if the values of a and b are substituted in it. The agreement is satisfactory in order of magnitude between the empirical $c_2 - c_1$ and the calculated $c_2 - c_1$. It indicates proportionality between $c_2 - c_1$ and $\frac{\sqrt{\rho_1}}{\eta}R$, but does not agree completely with the numerical factor for which Knudsen substitutes a value d. From the value for $\frac{c_1}{c_2}$ and the value for $c_2 - c_1$ containing d Knudsen deduces the values of c_2 and c_1, as

$$c_2 = d\,\frac{\sqrt{\rho_1}}{\eta}\,R$$

$$c_1 = 0.810d\,\frac{\sqrt{\rho_1}}{\eta}\,R,$$

$$T = \frac{\pi}{8}\,\frac{1}{\eta}\,\frac{R^4}{L}\,p + \frac{4}{3}\sqrt{2\pi}\,\frac{1}{\sqrt{\rho_1}}\,\frac{R^3}{L}\left(\frac{1 + 0.81d\frac{\sqrt{\rho_1}}{\eta}Rp}{1 + d\frac{\sqrt{\rho_1}}{\eta}Rp}\right).$$

This equation is now no longer completely empirical in the sense that all the constants are more or less rigorously deduced from theoretical considerations and are in no sense arbitrary. The only one approaching an arbitrary value is the constant d. Its numerical value was estimated from rough theoretical considerations only and hence is uncertain.

To obtain a more correct empirical value of d and to test the equation, the expression for T can be differentiated to find the value of p for the minimum of the curve. This leads to the expression for p_m, the pressure at the minimum:

$$p_m = \frac{\eta}{d\sqrt{\rho_1}R}\left(\sqrt{\frac{d \times 0.190}{m}} - 1\right) = \frac{1}{c_2}\left(\sqrt{\frac{d \times 0.19}{m}} - 1\right),$$

where $m = \frac{3\sqrt{\pi}}{32\sqrt{2}}$. From this it can be shown that the following conditions must hold. They are that

$$p_m c_2 = \text{constant}.$$

$$\frac{T_m}{T_0} = \text{constant } (T_0 \text{ is the value of } T \text{ when } p = 0).$$

$$\frac{R}{\lambda_m} = \text{constant}.$$

These conditions are tested on the empirical constants of his observations and found to hold. From the relation that $p_m c_2$ is a constant observed to be near unity, d is computed as 2.47. This value is checked by calculating $\frac{T_m}{T_0}$ and $\frac{R}{\lambda_m}$, using d from his equation for the minimum and comparing these with the observed values. They agree fairly well. If, then, these values be assumed, T, the outflow per unit pressure difference, is obtained as

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p + \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}\left(\frac{1 + 2.00\frac{\sqrt{\rho_1}}{\eta}Rp}{1 + 2.47\frac{\sqrt{\rho_1}}{\eta}Rp}\right)$$

or, expressed in terms of the mean free path,

$$T = \frac{Q_t}{p_1 - p_2} = \frac{\pi\sqrt{\pi}}{8\sqrt{8}(0.30967)}\frac{R^4}{L}\frac{1}{\lambda\sqrt{\rho_1}} + \frac{4}{3}\sqrt{2\pi}\frac{R^3}{L}\frac{1}{\sqrt{\rho_1}}\left(\frac{1 + 0.81\frac{5R}{\lambda}}{1 + \frac{5R}{\lambda}}\right).$$

Thus, with the aid of the kinetic-theory analysis at low pressures, one has a complete analysis of the flow of gases down a tube of cylindrical cross-section. In making this analysis, certain new concepts about the momentum exchanges between solid surfaces and the gas have also been derived.

79. The Effusion of Gases[12] and the Formation of Molecular Beams.[59]—Closely allied to the problem of the flow of rarefied gases through long tubes is the problem of the flow through short tubes and through holes in thin diaphragms. While for higher pressures and large openings the problem is one of fluid flow and belongs to the field of hydrodynamics, it becomes exceedingly simple at pressures below that at which the mean free path equals the linear dimensions of the openings. In addition it becomes possible to apply these phenomena to the production of molecular beams or rays in which the motion of molecules is confined to a single axis. Such beams are virtually devoid of molecular impacts if they traverse a gas-free space, so that they may be used to study the properties of molecules directly.

In order to discuss this problem, one must first take up the simple problem of effusion through a diaphragm of negligible thickness. Consider such a diaphragm with a hole of area A in it. On the one side of the hole there is a gas space with a pressure p_1 in it, while on the other side the pressure is p_2, such that $p_1 > p_2$. The linear dimensions of A are not larger than the mean free path of the gas molecules at either pressure and may be much smaller. The gas spaces S_1 and S_2 in which the pressures p_1 and p_2 obtain are so large that the molecules encounter each other more frequently than they do the walls. In Sec. 40 it was shown that the number of molecules striking unit area of a gas space in equilibrium was

$$\nu = \frac{N\bar{c}}{4} = \frac{p}{m}\sqrt{\frac{M}{2\pi R_0 T}} = \frac{p\sqrt{\rho_1}}{m\sqrt{2\pi}}.$$

Here N is the number of molecules per unit volume, $\bar{c}$ is the average velocity, p is the pressure in dynes per cm^2, M the molecular weight, R_0 the gas constant per mole, T the absolute temperature assumed the same on both sides of A, ρ_1 is the density per unit pressure p, and m the mass of a molecule. If the numbers of molecules per unit volume on the two sides of the diaphragm are N_1 and N_2, respectively, there are simultaneously bombarding the area A from opposite sides, $\frac{N_1\bar{c}}{4}A$ and $\frac{N_2\bar{c}}{4}A$ molecules per second. Since the pressures are quite low, and the hole of area A is small compared to the free path, all

the molecules striking from either side will get through. Thus the net molecular transfer will take place from the side where N is greater to that where it is less, *i.e.*, from S_1 to S_2. Hence n more molecules will go from S_1 to S_2 than in the reverse sense, where

$$n = \frac{1}{4}A(N_1 - N_2)\bar{c} = \frac{p_1 - p_2}{m}\sqrt{\frac{M}{2\pi R_0 T}}A = \frac{p_1 - p_2}{m}A\sqrt{\frac{\rho_1}{2\pi}}.$$

The mass flow G per unit time through area A is

$$G = nm = (p_1 - p_2)A\sqrt{\frac{M}{2\pi R_0 T}} = (p_1 - p_2)A\sqrt{\frac{\rho_1}{2\pi}},$$

and $Q_t = G/\rho_1$ becomes

$$Q_t = \frac{(p_1 - p_2)A}{\sqrt{2\pi}\sqrt{\rho_1}}.$$

It is clear from this that Q_t varies as $p_1 - p_2$, as A, inversely as the square root of the molecular weight and directly as the square root of the absolute temperature. If $p_2 = 0$ as would be the case for effusion into a good vacuum, Q_t varies directly as p_1. The rate of effusion calculated above depends on the equation $\nu = N\bar{c}/4$ which is deduced on the basis of the Maxwellian distribution of velocities.* Hence the numerical factor $1/\sqrt{2\pi}$ in the expression for Q_t depends on the distribution of velocities. If all the molecules had equal velocities, the numerical coefficient would have differed from this quantity by 8.6 per cent. Knudsen measured the velocity of effusion for H_2, O_2, and CO_2 estimating the quantity $Q_t/(p_1 - p_2) = T$ to within 3 per cent, which was the accuracy to which he could measure A. The values obtained were in agreement with the theoretical expression to within 3.5 per cent, thus in a measure establishing the law for the distribution of velocities.

In order to consider further the flow of rarefied gases down tubes of short length, and the formation of molecular beams, one must consider the general method developed by H. A. Lorentz[60] for the calculation of the flow of rarefied gases through

* This statement holds for the equation deduced in Sec. 40 and the expression $N\bar{c}/4$. It will be seen in Sec. 81 that a law expressing the same condition, that the number of molecules striking unit area per second is $Nu/4$ where u is the average velocity, is much more general and holds for any distribution law requiring only the cosine law of reflection from the walls.

tubes. This deduction is more rigorous than Knudsen's deduction for a long tube and is capable of an extension to short tubes, for which the end corrections are of necessity quite important in the Knudsen method. The general method of Lorentz was extended by P. Clausing[61] to the general problem with the results to be detailed later.

Lorentz starts by assuming pressures so low that impacts between the molecules can be neglected relatively to impacts against the walls. He further assumes molecular roughness at the walls such that molecules striking the walls are reflected from them with all past history of motion eradicated, *i.e.*, he assumes for such impacts that Maxwell's f equals unity. He then considers the exchange of molecules between two surface areas $d\sigma$ and $d\sigma'$ so oriented that the line of length r joining their centers p and p' makes angles θ and θ' with the normals to the elements. Since the emission from these rough surfaces for which $f = 1$ follows the cosine law, one can write in analogy to the conditions in a furnace in black-body radiation that

$$B \cos \theta d\omega d\sigma = B \cos \theta' d\omega' d\sigma' = B \cos \theta' d\sigma' \frac{d\sigma \cos \theta}{r^2}.$$

Here B depends on the total number of molecules reflected from unit area per second which in equilibrium is the same as strike it per second; $d\omega$ and $d\omega'$ are respectively the solid angles subtended by $d\sigma'$ and $d\sigma$ at the centers of $d\sigma$ and $d\sigma'$; and r is the distance between the centers of $d\sigma$ and $d\sigma'$. Hence, if the walls are at constant temperature, the space filled with a rarefied gas is in equilibrium and B is for all wall elements the same. Thus the expression above given holds not only for the emission from surface elements but must hold equally well for the number of particles which pass through an area of the gas occupied by the surface elements. This enables B to be at once determined. Consider the number of particles whose direction of motion falls within a cone $d\omega$ whose axis is normal to $d\sigma$, which pass through the area $d\sigma$. This number is obviously $Bd\sigma d\omega$, as $\theta = 0$. If $f(v)dv$ is the number of molecules per unit volume whose velocity lies between v and $v + dv$, one can write at once that

$$\frac{d\omega}{4\pi} d\sigma \int_0^\infty v f(v) dv = B d\sigma d\omega.$$

Integration, assuming Maxwell's distribution of velocities, at once yields

$$B = \frac{p}{m\pi}\sqrt{\frac{M}{2\pi R_0 T}} = \frac{N\bar{c}}{4\pi}.$$

In this respect it is to be noticed that the quantity B is not the same as ν, the number of molecules striking a cm^2 per second but is related to it by $B = \nu/\pi$. The relationships just deduced enable one to attack the problems of the flow in tubes by considering the net transfer from a surface element of tube through a plane area at right angles to the axis of the tube, and by integration over appropriate limits to calculate the flow in any form of tube.

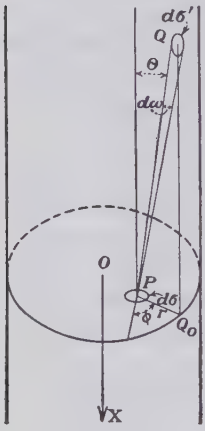

FIG. 48.

Assume the vertical tube shown in Fig. 48 with a pressure gradient *down* the tube which maintains the flow. If then B_Q be the value of B at some surface element of area $d\sigma'$, located at Q in the tube, the value of B at a cross-sectional plane OPQ_0, x cm down the tube due to the pressure gradient will be given by $B = B_0 - x\dfrac{dB}{dx}$. One may then consider the exchange of molecules between the wall element $d\sigma'$ and an element $d\sigma$ of the cross-sectional area at O, OPQ_0. The element $d\sigma$ is at a distance r cm from the foot of the normal to OPQ_0 passing through $d\sigma'$. Hence the normal to $d\sigma$ makes an angle θ with QP at $d\sigma$ and an angle of $90 - \theta$ with the normal to $d\sigma'$ at $d\sigma'$. Furthermore, $d\omega$ is the solid angle subtended at the center of $d\sigma$ by $d\sigma'$, and $d\omega'$ is the solid angle subtended by $d\sigma$ at the center of $d\sigma'$. The distance x between the cross section at $d\sigma$ and that at $d\sigma'$ is then $x = r \cot \theta$, where r is the distance of $d\sigma$ from the wall at a point directly below $d\sigma'$. Hence $B_Q = B + r \cot \theta \dfrac{dB}{dx}$. Under these conditions $B_Q \cos \theta' d\omega' d\sigma' = B_Q \cos \theta d\omega d\sigma$.

One may accordingly compare the flow due to $d\sigma'$ through $d\sigma$ with the flow through $d\sigma$ headed for $d\sigma'$. The flow from $d\sigma$ is $B \cos \theta d\omega d\sigma$, while that from $d\sigma'$ is $B_Q \cos \theta d\omega d\sigma = B \cos \theta d\omega d\sigma + (dB/dx)r \cos \theta \cos \theta d\omega d\sigma$. Thus the net transfer from above is given by $(dB/dx)r \cos \theta \cot \theta d\omega d\sigma$. If this is integrated

over both hemispheres about the cross section with respect to $d\omega$, one gets the whole flow for an infinitely long tube. It is simpler to multiply the expression by two and integrate over the upper hemisphere. Thus the net flow through $d\sigma$ is

$$2\frac{dB}{dx}d\sigma\int r\cos\theta\cot\theta d\omega,$$

which can be integrated by setting $d\omega = \sin\theta d\theta d\phi$, where ϕ is an angle of rotation in the plane measured from r and about $d\sigma$ as axis. Then making $d\sigma$ a ring of area $2\pi ldl$ where l is the distance from the axis of the tube to $d\sigma$, integration gives D, the number of molecules flowing through a cross section of the cylindrical tube of radius R and length L per second as

$$D = \frac{8}{3}\pi^2R^3\frac{dB}{dx} = \frac{8}{3}\pi^2\frac{R^3}{m\pi}\sqrt{\frac{M}{2\pi R_0T}}\frac{(p_1 - p_2)}{L},$$

or

$$G = \frac{8}{3}\pi\frac{R^3}{L}(p_1 - p_2)\sqrt{\frac{\rho_1}{2\pi}}$$

in agreement with Knudsen's equation.

Clausing,[61] in his study, approaches the problem from the same general point of view. He, however, rearranges the equations in a more suitable fashion. Starting with the general Knudsen equation for the volume flow, and $p_2 = 0$, he writes

$$Q_t = \frac{G}{\rho_1} = \frac{p}{\sqrt{\rho_1}W} = \left(\frac{p}{\sqrt{2\pi\rho_1}}\right)AP,$$

where A is the area of cross section and P is defined by $P = \sqrt{2\pi}/AW$. The number of molecules K emerging from the end of a tube of cross section A per second is then given as

$$K = \frac{Q_t\rho_1}{m} = \frac{\sqrt{\rho_1}p}{mW}.$$

Now ν, the number of molecules effusing out of a hole of unit area per second, was shown to be

$$\nu = \frac{p}{m}\sqrt{\frac{M}{2\pi R_0T}} = \frac{p}{m}\sqrt{\frac{\rho_1}{2\pi}},$$

whence

$$K = \frac{\sqrt{\rho_1}p}{mW} = \frac{\sqrt{2\pi}A\nu}{AW} = PA\nu.$$

Thus the number of molecules emerging from a tube of area A is ν, the number effusing through unit area per second, times the area A multiplied by a factor P. This P is less than unity for a tube of finite length and varies with the form and dimensions of the tube. Clausing[61] develops the methods for calculating P for a large number of cases and, in an article in *Physica*, assembles those evaluated to date. These are given below:

1. A hole in an infinitely thin diaphragm gives $P = 1$.
2. A long cylindrical tube, length L, radius R, $L >> R$, $P = \frac{8}{3}\frac{R}{L}$.
3. A long slit-like tube of length L, depth a, breadth b, where $a >> L >> b$, $P = \frac{b}{L}\log\frac{b}{L}$.
4. A long rectangular tube of length L, depth a, breadth b, $L >> a$, $L >> b$,

$$P = \frac{1}{Lab}\left\{a^2b\log\left[\frac{b}{a} + \sqrt{1 + \left(\frac{b}{a}\right)^2}\right] + ab^2\log\left[\frac{a}{b} + \sqrt{1 + \left(\frac{a}{b}\right)^2}\right] - \frac{(a^2 + b^2)^{3/2}}{3} + \frac{a^3 + b^3}{3}\right\}.$$

5. Short cylindrical tubes of ratio of length L to radius R as follows:

L/R	P	L/R	P
0	1.000	1.5	0.5810
0.1	0.9524	2.0	0.5136
0.2	0.9092	3.0	0.4205
0.4	0.8341	4.0	0.3589
0.5	0.8013	8.0	0.2316
0.8	0.7177	10.0	0.1973
1.0	0.6720	100.0	0.0258
		∞	$8R/3L$

6. Short slit-like tube $a >> b$, $a >> L$.

L/b	P	L/b	P
0.0	1.000	1.0	0.6848
0.1	0.9525	2.0	0.5417
0.2	0.9096	3.0	0.4670
0.4	0.8362	4.0	0.3999
0.8	0.7266	5.0	0.3582
		10.0	0.2457

In generating a molecular beam the molecules are confined in a vessel of dimensions large compared to the mean free path at a constant pressure, *i.e.*, by heating the solid or liquid sub-

stance at a constant temperature or by connecting it to a large reservoir at constant temperature. This vessel is provided with a slit or a tube of one of the types described above, whose breadth at least is of the order of, or smaller than, the mean free path. This is termed the *fore slit* or *source slit.* The escaping molecules expand out of this slit into a space which is maintained at as low a pressure as possible by very rapid pumping. The molecules emerging from the fore slit emerge in all directions according to laws which will be discussed later. Of those emerging, a certain number of molecules are selected out, going in the desired direction within a given solid angle by a *second* or *image slit.* It is this beam that is used for various purposes.

It is essential in all designs of molecular beam devices to be able to calculate the number of molecules within the molecular beam as well as the shape of the beam resulting. If one has a true molecular beam, one can, using the geometrical constructions of optics, at once delineate the shape of the *umbra* and *penumbra* of the molecular beam at any distance from the image slit, given the dimensions of the image and fore slit and the distance r between them. This follows at once from the rectilinear paths in a true molecular beam. As regards the number of molecules in the beam, the calculations require a study of the laws of emission of molecules from a hole or the orifice of a tube, which will be given in the following paragraphs.

Before proceeding, a word of caution is necessary. That is, that in order to have a true molecular beam the *pressure* in the source must be such that the mean free path is not, at the very least, less than half the width of the slit. It should be less than this for the best results. If this is not complied with, molecules emerging will collide within the slit and just beyond it. This leads to what Knauer and Stern term a *cloud* formation. Thus the emerging molecules will have collisions between fore and image slits. This makes the effective area from which the molecules going through the image slit originate larger than the fore slit. It thus results in the rounding off of the otherwise geometrical images of the slits. Practically, it has been found that one can have the free path about half the fore slit without too much cloud formation. Beyond this, one can rely no more on the beam as a true molecular beam.

To consider the angular distribution of the emitted molecules, one must begin with the distribution for the case of a hole in an

infinitely thin diaphragm, *i.e.*, with the case of effusion. For a hole of area A the *total emission* was found to be

$$Q_t = \frac{A}{\sqrt{2\pi}} \frac{p_1 - p_2}{\sqrt{\rho_1}} \text{ and } G = \frac{A}{\sqrt{2\pi}} \sqrt{\rho_1}(p_1 - p_2).$$

One may now study the distribution in angle. Inside the oven a molecule starting for the surface A at an angle θ with the normal will emerge with a velocity making an angle θ with the outside normal. But the number emerging is proportional to the area of the opening normal to their direction of motion. Thus for the molecules emerging at θ the area available is $A \cos \theta$. Hence the mass of molecules emerging within a solid cone $d\omega$ at an angle θ with the normal to A will be proportional to $A \cos \theta$, to the mass of molecules G/A striking unit surface per second, and to the ratio of the solid angle of the cone to the solid angle embracing all the emergent molecules. Hence one can write

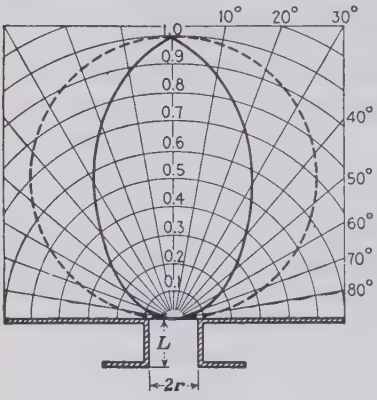

FIG. 49.

$$G_\theta = D\frac{G}{A} A \cos \theta \frac{d\omega}{2\pi} = DG\frac{d\omega}{2\pi} \cos \theta.$$

Here D, the constant of proportionality, is determined at once by the relations,

$$\int_0^{\frac{\pi}{2}} G_\theta d\theta = G \text{ and } d\omega = 2\pi \sin \theta d\theta.$$

Whence

$$\int^{\frac{\pi}{2}} \frac{GD2\pi \sin \theta \cos \theta d\theta}{2\pi} = \frac{DG}{2}, \text{ or } D = 2.$$

Thus the mass of molecules emerging at an angle θ with the normal is

$$G_\theta = 2G\frac{d\omega \cos \theta}{2\pi} = \frac{Gd\omega \cos \theta}{\pi},$$

and the number at θ is

$$K_\theta = \frac{G_\theta}{m} = A\nu \cos\theta \frac{d\omega}{\pi}.$$

The distribution in G or K with angle may be plotted in polar coordinates. In this case G_θ is the radius vector using a given value of $A\nu$ and $d\omega$, and θ is measured from the normal to the surface. The curve obtained is a circle about G as diameter, as seen in Fig. 49. It is seen that the number of molecules emitted in a forward direction is the greatest and that it is 0 at $\theta = \pi/2$. Clausing[61] has worked out the distribution of K_θ for the case of a short tube for which $L = 2R$. In this case the table on page 306 shows that the value of K for the total outflow is given by $K = 0.514A\nu$, since $P = 0.514$. That is, the total gas flow is about one-half that for a hole of the same area A. For various angles the expression for $K_\theta = A\nu P' \cos\theta \frac{d\omega}{\pi}$, where P' takes on a series of values which decrease as θ increases. A plot of K_θ in polar coordinates is shown in the egg-shaped curve of Fig. 49. The quantity $P' \cos\theta \frac{d\omega}{\pi}$ in this case is equivalent to the expression $\cos\theta \frac{d\omega}{\pi}$ in the case of the hole. It is seen that, for $\theta = 0$, $P' \cos\theta = 1$ if $d\omega/2\pi$ is chosen small enough. Hence in this case the outflow in the forward direction is as great as for a hole in a thin diaphragm. Even at $\theta = 10°$, $P' \cos\theta = 0.88$, so that an angular beam of considerable width through a short tube gives nearly *the same flow in a forward direction* as a hole of the same area. This point is of considerable interest in that, by using a tube of this sort, the distribution in a forward direction (*i.e.*, in the direction needed for the beam) is nearly equal to that for a hole while the total gas escaping is reduced to one half. This makes it possible to increase the outflow from the slit without spoiling the vacuum between oven and image slits. Clausing shows that it is probable that with a greater ratio of L to R, one can expect a still greater increase in forward intensity relative to the total outflow.

Before leaving the question of the formation of molecular beams, it pays to develop the equations into such a form that they enable one readily to calculate the intensity in a given molecular beam.

For a hole in a diaphragm of area A the number of molecules K_θ escaping at an angle θ in a cone of solid angle $d\omega$ is

$$K_\theta = \frac{1}{m}\sqrt{\frac{M}{2\pi R_0 T}} Ap \cos\theta \frac{d\omega}{\pi}$$
$$= \frac{N_A}{\sqrt{2\pi R_0 MT}} pA \cos\theta \frac{d\omega}{\pi} \text{ molecules per second.}$$

For a cylinder of radius $L = 2R$,

$$K_\theta = \frac{N_A}{\sqrt{2\pi R_0 MT}} pAP' \cos\theta \frac{d\omega}{\pi}.$$

In terms of moles per second the value for the hole is

$q = \dfrac{1}{\sqrt{2\pi R_0 MT}} pA \cos\theta \dfrac{d\omega}{\pi}$ moles per second, if p is in dynes per cm^2;

$q = \dfrac{5.83 \times 10^{-2}}{\sqrt{MT}} p_2 A \cos\theta \dfrac{d\omega}{\pi}$ moles per second, if p_2 is in mm of Hg.

In using these equations it is to be noted that N_A is the Avogadro number, m the mass of the molecules, M their molecular weight, R_0 the gas constant per mole, T the absolute temperature, p the pressure in the source in dynes per cm^2, A the slit area in cm^2, $d\omega$ the area of the image slit in cm^2 divided by r^2, the square of the distance of the image slit from the source in cm. The angle θ represents the direction of the beam from the normal to the source slit, and the image slit is assumed to be normal to the direction of the beam. P' for the tube can be found from the curve of Fig. 49 as a function of θ. For other tubes, only the quantity P for total emission relative to a hole has been calculated. If the image slit be placed on the axis ($\theta = 0$) of the tube, it is clear that the pointed nature of the beam will make the emitted amount in this direction relatively greater than would be the case for the hole, and, if the tube be made of reasonable length, it is probable that a beam of good intensity can be obtained with few diffuse molecules.

80. Heat Conduction at Low Pressures.—When the consideration of heat conduction at low pressures is begun, as was stated in Sec. 76, the importance of the transfer of heat from and to the surfaces becomes greatly enhanced. Let the discussion first be extended to the mechanism of heat transfer from gas to solid

irrespective of the pressure. Assume a metal surface at one temperature and the gas at a uniform higher temperature. Heat then passes from the hot gas to the cooler metal by the following mechanism: If the gas has the same temperature T_1 throughout, molecules having a velocity appropriate to the temperature, on the average, start from a layer one mean free path away and strike the surface at a rate $N\bar{c}/4$ per cm^2 per second, where N is the number of molecules per cm^3 and $\bar{c}$ the average velocity. Each of these carries an energy corresponding to its specific heat. If it be assumed that there is no specular reflection and that all molecules striking the surface attain thermal equilibrium with it, these molecules leave the surface with the lower velocity corresponding to T_2, the temperature of the metal. From this consideration the rate of heat transfer from the gas to the solid can be computed. If it be assumed that this transfer takes place across the distance of a mean free path, a coefficient of heat conductivity from gas to solid can be estimated by taking the temperature gradient as $\frac{T_1 - T_2}{L}$. The value thus computed is, however, a hundred fold or even more than that computed from actual observed heat transfers. This has led some writers, especially in the engineering field, to postulate a heat-insulating layer, or a layer of lowered heat conductivity in the gas next the solid. Such a picture is distinctly misleading and even wrong. The fact that the molecules leave the surface at a temperature T_2 at once furnishes a clue to the question, for these molecules collide in their first free path with the molecules of the gas T_1. Since they must be nearly equal in number in the first free path, collisions here result in a redistribution of energy, so that the average temperature in this layer is not T_1 or T_2 but has an intermediate value. As the molecules leaving the surface make more and more impacts, they acquire more nearly the temperature of the gas T_1. Thus the temperature gradient does not exist right up to the last free path from the surface, but the gradient extends over many free paths, perhaps even as many as 100 free paths from the surface. It is the existence of this gradient which limits the rate of heat transfer to the surface. In attempting to increase the heat conductivity it is necessary to increase this gradient. This could only be accomplished by removing the cool molecules to the interior of the gas as soon as they leave the surface and supplying new hot ones to replace them. It seems

possible that by setting the gas into a violent mass motion one could accomplish this (*i.e.*, by the use of hot blasts of gas). If, however, one considers that the blast velocities usually achieved are small compared with thermal velocities which would be required to remove the cooled molecules from the surface, the futility of this method is at once seen. Furthermore, the absence of slip at higher pressures makes this difficult, for the gas has a sharp velocity gradient near the surface. If it were possible to generate a *molecular* turbulence at or near the surface, the difficulty might be in part overcome. Thus far, no success has been achieved in this direction. The "insulating layer" at the surface is therefore nothing but the slowly moving (stagnant) layer of gas near the surface in which a gradual temperature gradient is set up by heat interchanges of a kinetic nature among the gas molecules.

As the pressures are reduced, however, these conditions rapidly change, for as soon as the mean free path becomes very great the slip for moving gases manifests itself. But more important than the slip is the fact that in the exchange of heat through the gas from a heated surface to a cooler one the molecules leaving the cooler surface do not meet enough heated molecules to get into equilibrium with them, before they reach the hotter surface heating the gas. Thus, the problem of heat conduction at low pressures at once involves not only the conduction from gas to solid surface, but rather the transfer from one surface to the other by means of the gas molecules. Furthermore, since the molecules now cross from one surface to the other before reaching equilibrium, it is obvious that, instead of the gradual transition of temperature from one surface to the gas, appearing to exist at higher pressures, there is an abrupt change of temperature from surface to the gas, whose value can be measured. It is this marked temperature drop at the solid gas surface that is the feature of the low-pressure heat-conduction phenomenon.

The existence of this drop was first postulated by Kundt and Warburg[2] as a result of the considerations following from their work on the flow of gases through tubes at low pressures, for, with molecules leaving the surface at the temperature of the surface and exchanging energy with the rest of the gas at the first impact, the first layer of gas one free path away must be warmer than the solid. At high pressures a free path is so small that it cannot be detected, but as the free paths become larger the gradient must

come to light. Von Smoluchowski[13] investigated this experimentally and found it to exist. He found, however, that it was greater for H_2 than for air. This he interpreted as meaning that the H_2 molecules, because of their small mass, exchanged less momentum with the molecules of the surface, and thus retained more of their initial energy than the air molecules did. Thus, the gradient at the surface was steeper in H_2 than in air. Certain experiments of Knudsen[14] on the absolute manometer and other low-pressure phenomena led him to conclude that apparently the rebounding gas molecules from a solid surface did not reach temperature equilibrium with the surface. In his case, H_2 also showed the strongest departure from the anticipated behavior. A somewhat similar conclusion was also arrived at by Soddy and Berry,[15] who investigated the heat conductivity of various gases at higher pressures and found that the lower the specific gravity of a gas the more their results departed from the theoretically expected value. Knudsen therefore decided that these departures from anticipated laws needed more extended investigation. Since, however, the theory of heat conductivity at higher pressures was not altogether successfully solved theoretically, Knudsen[16] felt that an investigation of these deviations at lower pressures where simpler theoretical laws obtain, and the deviations are even greater, would prove of value. In a masterful experimental investigation accompanied by a theoretical investigation he sets forth the conclusions which he draws. The interpretations of his results are called into question by von Smoluchowski[17] in a later theoretical paper. As will be seen, the objections raised by von Smoluchowski deal only with certain details of Knudsen's work. In fact, he accepts the general point of view of Knudsen as more satisfactory for very low pressures than his own. Later work of Knudsen still further establishes the correctness of his point of view. The work of Knudsen will thus be given.

The theory of Knudsen proceeds as follows: He assumes two parallel plates A_1 and A_2 opposite each other, and that they have *absolutely rough* surfaces. That is, that they have surfaces which are so constructed that when molecules strike them they bound back and forth enough times in the pores of the surface that they acquire the temperature of the surface on leaving. This assumption is really something more than the assumption of the *random direction of emergence*, when the particles leave the surface, first

made by Maxwell in explaining slip, for in a random direction of emergence but one or two impacts are needed with the surface, while to gain thermal equilibrium with the surface the molecule must make many more impacts. Call T_1' and T_2' the temperatures of the two surfaces, and $\bar{c}_1$ and $\bar{c}_2$ the average velocities of the molecules leaving A_1 and A_2. It is further essential to assume that the molecule of mass m and velocity c has an energy $\frac{1}{2}mc^2$ only. This means that if one has a molecule not an atom, one must, for simplicity, first regard only its translatory energy, and leave out the other forms of rotational or vibrational energy, for it is obvious that these energies may enter into the exchanges in a different fashion from the translational energy. The latter can be introduced into the discussion at a later point.

As the molecules leaving A_1 have one velocity c_1 while those leaving A_2 have another value c_2, the equilibrium conditions will have to be differently formulated. Assume dN_1 molecules of velocity components between c_1 and $c_1 + dc_1$ *directed away from* A_1. These will strike A_2. If there were dN molecules per cm^3 having *all* directions relative to A_1, then $\frac{1}{4}dNc_1$ molecules would strike 1 cm^2 of A_2 per second. But $dN/2 = dN_1$ by the definition of dN_1, therefore $\frac{1}{2}dN_1c_1$ molecules strike the cm^2 of A_2 per second. Similarly, $\frac{1}{2}dN_2c_2$ molecules of velocity between c_2 and $c_2 + dc_2$ having their velocities directed away from A_2 will strike a cm^2 of A_1 per second. Thus, if the molecules striking A_2 did not emerge again from A_2, the energy gain of A_2 would be $dE_1 = \frac{1}{2}dN_1c_1\left(\frac{1}{2}mc_1^2\right)$. Hence $E_1 = \frac{1}{4}m\int_{c_1=0}^{c_1=\infty} c_1^3dN_1$. From Maxwell's distribution law,

$$dN_1 = \frac{4N_1}{\alpha_1^3\pi^{\frac{1}{2}}}c_1^2e^{-\frac{c_1^2}{\alpha_1^2}}dc_1,$$

whence

$$E_1 = \frac{1}{4}m\frac{4N_1\alpha_1^3}{\sqrt{\pi}}.$$

This at once is converted to the form $E_1 = \frac{\pi}{8}mN_1\bar{c}_1^3$. In a similar manner $E_2 = \frac{\pi}{8}mN_2\bar{c}_2^3$. Now E_1 is received by A_2 per cm^2 per second and E_2 is given up to A_1 from A_2. As the areas

are equal, the net gain E_T of translational energy by A_2 per cm^2 per second must be $E_1 - E_2$. Thus the gain of energy of A_2 is

$$E_T = \frac{\pi}{8} m(N_1 \bar{c}_1^3 - N_2 \bar{c}_2^3).$$

Now the molecules that strike A_2 per cm^2 per second, if there are N_1 molecules of average velocity $\bar{c}_1$ with velocity components towards A_2 per cm^3, are $N_1\bar{c}_1/2$. In a similar fashion the number that strike A_1 is $N_2\bar{c}_2/2$. As the molecules leaving these surfaces must equal those arriving when equilibrium is established and no molecules escape from between the plates,

$$\frac{1}{2} N_1 \bar{c}_1 = \frac{1}{2} N_2 \bar{c}_2.$$

Again, if the two plates be surrounded by gas molecules at an average speed $\bar{c}$ and there are N of these per cm^3 in order that the pressure between the plates remain constant, the number of molecules passing out through the edges from between the plates must equal the number passing inward from outside. If E be the area at the edges the equilibrium is established when $\frac{1}{4} N_1 \bar{c}_1 E + \frac{1}{4} N_2 \bar{c}_2 E = \frac{1}{4} N \bar{c} E$, or $2N_1\bar{c}_1 = N\bar{c}$,

whence

$$N_1 \bar{c}_1 = N_2 \bar{c}_2 = \frac{N\bar{c}}{2}.$$

The expression for E_T then becomes

$$E_T = \frac{\pi}{16} N m \bar{c} (\bar{c}_1^2 - \bar{c}_2^2).$$

Since

$$\bar{c} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{T}{273} \frac{1}{\rho_0}}$$

where T is the absolute temperature and ρ_0 is the specific gravity of the gas at 273° abs. and a pressure 1 dyne per cm^2, then

$$E_T = \sqrt{\frac{2}{\pi}} p \frac{1}{\sqrt{\rho_0}} \frac{T_1 - T_2}{\sqrt{273T}},$$

where the analogous expressions for $\bar{c}_1$ and $\bar{c}_2$ are introduced and p is the pressure in dynes per cm^2 in the space between the plates. Thus the energy transferred from A_1 to A_2 per cm^2 per second is in terms of the pressure of the gas and the temperatures T_1 and T_2 of A_1 and A_2, and the temperature T of the gas.

This was deduced on very simple assumptions. Among others, attention was focused only on the transfer of translatory energy. If now rotational energy also contributes to heating the plates, then it must be included. The ratio k of the translational e_1, and rotational e_2, energies to the translational energy alone is $k = \frac{e_1 + e_2}{e_1}$. This, in turn, can be placed equal to $\frac{\frac{2}{3}c_v}{c_p - c_v}$, for, from Sec. 91,

$$\gamma = \frac{c_p}{c_v} = \frac{\frac{2}{3} + \frac{e_1 + e_2}{e_1}}{\frac{e_1 + e_2}{e_1}},$$

whence

$$(\gamma - 1)\frac{e_1 + e_2}{e_1} = \frac{2}{3}$$

and

$$k = \frac{e_1 + e_2}{e_1} = \frac{\frac{2}{3}}{(\gamma - 1)}.$$

Now so far in the theory $e_1 = \frac{1}{2}mc^2$, the translational energy alone has been used in the heat transferred to A_2. Actually, $e_1 + e_2$ is transferred by each molecule. This would mean that $k(\frac{1}{2}mc^2)$ gives the energy transferred by each molecule, provided it is assumed that *for each molecule* $e_2 = (k - 1)e_1$ as the equation demands. The correct value of E_T would then be multiplied by the factor $k = \frac{\frac{2}{3}}{(\gamma - 1)}$, where γ is the ratio of the specific heats.

This treatment does not satisfy Knudsen, for he states that, while, on the average, in impact between molecules the net relative values of rotational and translational energies may not be altered, the relative values in each molecule are changed after the encounter. He assumes that the two quantities are distributed independently among the molecules, but that, on the average, they bear a definite ratio to each other. This requires that the value of E_T be redetermined averaging the rotational energies separately under this assumption. A_2 receives $\frac{1}{2}dN_1c_1$ impacts per cm² per second. Each impacting molecule carries the energy $\frac{1}{2}mC_1^2$, where C_1^2 is the *average squared velocity*. Since $e_2 = (k - 1)e_1$ then the rotational energy carried is $\frac{1}{2}mC_1^2(k - 1)$, and the energy transfer per cm² per second due to rotational or vibrational energies is

$$dE_1' = \frac{1}{4}mC_1^2(k-1)c_1dN_1$$

$$E_1' = \frac{1}{4}mC_1^2(k-1)\int_{c_1=0}^{c_1=\infty} c_1dN_1$$

$$= \frac{1}{4}mC_1^2(k-1)\bar{c}_1N_1.$$

Accordingly, this treatment differs from the translational case in that one computes $C_1^2\int_{c_1=0}^{c_1=\infty} c_1dN_1$ here, while before one computed $\int_{c_1=0}^{c_1=\infty} c_1^3dN_1$. In this case the rotational velocities are averaged independently of translation. Likewise the rotational energy lost by A_2 is $E_2' = \frac{1}{4}mC_2^2(k-1)\bar{c}_2N_2$. Thus E_A, the total transfer due to rotational energy is, on reduction, as before,

$$E_A = \frac{3}{4}\sqrt{\frac{2}{\pi}}(k-1)p\frac{1}{\sqrt{\rho_0}}\frac{T_1-T_2}{\sqrt{273T}}.$$

The total energy carried is $E_T + E_A = E$, whence

$$E = \sqrt{\frac{2}{\pi}}\left\{1 + \frac{3}{4}(k-1)\right\}p\frac{1}{\sqrt{\rho_0}}\frac{T_1-T_2}{\sqrt{273T}}.$$

Putting in the value of k in terms of γ and putting for ρ the quantity $\frac{1409.2}{32} \times 10^{-12}M$, where M is the molecular weight, then

$$E = 1819.2\frac{\gamma+1}{\gamma-1}p\frac{T_1-T_2}{\sqrt{MT}} \text{ in ergs.*}$$

Practically, E cannot be directly measured conveniently due to radiation and residual gases. By measuring E at two pressures for a given $T_1 - T_2$, Knudsen gets a quantity $\epsilon = \Delta E/(\Delta p \Delta T)$ which has the value

$$\epsilon = 1819.2\frac{\gamma+1}{\gamma-1}\frac{1}{\sqrt{MT}} \text{ in ergs.}$$

Thus for H_2, O_2, and CO_2, putting in the values of Lummer and Pringsheim for γ, one has

* As will later be seen, while von Smoluchowski[17] agrees with the value for E_T, he gives reasons for believing that E_A is not correctly computed. It is in any case an approximation and a change in averaging will change E_A only a little numerically.

H_2 $\epsilon = 10.968 \times 10^{-6}\sqrt{\frac{273}{T}}$ gram-cal.

O_2 $\epsilon = 2.803 \times 10^{-6}\sqrt{\frac{273}{T}}$ gram-cal.

CO_2 $\epsilon = 3.045 \times 10^{-6}\sqrt{\frac{273}{T}}$ gram-cal.

As earlier experiments by others had intimated, Knudsen found the values of ϵ in these gases less than the theoretical value. This he interpreted as meaning that the molecules leaving A_1 are colder than T_1 and that those leaving A_2 are warmer than T_2, as they have not reached thermal equilibrium with the surfaces before being diffusely reflected. This might be classified by saying that the surfaces are not completely *molecularly rough*, and the term *molecular roughness* would then apply in the measure that the equations were fulfilled. In practice, therefore, the case for surfaces which are not molecularly rough must be considered. To take this into account, assume that $\bar{c}_1$ and $\bar{c}_2$ are the velocities of the molecules moving between the plates, $\bar{c}_1$ those going to A_2 and $\bar{c}_2$ those going to A_1. If the molecules had been in thermal equilibrium with the surface they had just left, then they would have had the velocities $\bar{c}_1'$ and $\bar{c}_2'$. If one can write that $\bar{c}_1^2 - \bar{c}_2^2 = \beta(\bar{c}_1'^2 - \bar{c}_2'^2)$, the equation for translatory energy exchange E_T' becomes

$$E_T' = \frac{\pi}{16} N m \bar{c} \beta (\bar{c}_1'^2 - \bar{c}_2'^2).$$

Since $\bar{c}_1'^2 - \bar{c}_2'^2$ determines the temperature difference $T_1' - T_2'$ in the same manner as $\bar{c}_1^2 - \bar{c}_2^2$ determined $T_1 - T_2$, one can write simply $E_T' = \beta E_T$. Thus the coefficient of heat conductivity ϵ_1 between not completely roughened surfaces is related to the coefficient of conductivity between completely *molecularly rough* surfaces ϵ by the expression

$$\epsilon_1 = \beta\epsilon = \frac{\bar{c}_1^2 - \bar{c}_2^2}{\bar{c}_1'^2 - \bar{c}_2'^2}\epsilon.$$

Actually, it is necessary to investigate the changes at the surface in order to get a theoretical expression for β. The average velocity $\bar{c}_1$ is not uniquely determined by $\bar{c}_1'$, the temperature velocity for equilibrium, with T_1', the temperature at A_1. It

also depends on $\bar{c}_2$, the temperature which the molecule had when it struck A_1. This relation could be expressed by

$$\bar{c}_1 = a\bar{c}_1' + b\bar{c}_2,$$

where a and b are constants. These must be so determined that when $\bar{c}_1' = \bar{c}_1$ and $\bar{c}_1 = \bar{c}_2$, the equations hold true, that is, $b = 1 - a$, for then $\bar{c}_1 = a\bar{c}_1' + (1 - a)\bar{c}_2 = (1 - a + a)\bar{c}_1$. Accordingly,

$$\bar{c}_1 = \bar{c}_2 + a(\bar{c}_1' - \bar{c}_2).$$

For plates large in dimensions compared to the distance between them, and whose surfaces are the same, a must be the same for both surfaces, and one can write

$$\bar{c}_2 = \bar{c}_1 + a(\bar{c}_2' - \bar{c}_1).$$

The addition of these two equations gives $\bar{c}_1 + \bar{c}_2 = \bar{c}_1' + \bar{c}_2'$, an equation which Knudsen had confirmed experimentally in earlier work. Subtraction of the two expressions gives $\bar{c}_1 - \bar{c}_2 = \frac{a}{2 - a}(\bar{c}_1' - \bar{c}_2')$. Multiplying the two expressions, then

$$\bar{c}_1^2 - \bar{c}_2^2 = \frac{a}{2 - a}(\bar{c}_1'^2 - \bar{c}_2'^2).$$

Thus β has the value $\beta = \frac{a}{2 - a}$. The fraction a of the velocity equivalent to the temperature of the surface which the molecule carries away with itself on leaving the surface is called the *coefficient of accommodation*. The heat conductivity between two large parallel similar surfaces is then given by

$$\epsilon_{11} = \frac{a}{2 - a}\epsilon = 43.46 \times 10^{-6}\left(\frac{a}{2 - a}\right)\frac{\gamma + 1}{\gamma - 1}\frac{1}{\sqrt{MT}} \text{ gram-cal.}$$

Thus if ϵ_{11} is measured, a can be determined.*

In practice, it is not easy to measure ϵ_{11}. There is, however, a very interesting case, and that is where one of the surfaces is a fine cylindrical wire and the other a concentric cylindrical surface about it. In this case the molecules strike the outer surface a great many times compared with the inner surface. The mole-

* This equation is of the same form as one independently derived by von Smoluchowski[17] from similar assumptions, and appears to be the correct form. The ϵ used by von Smoluchowski, however, does not contain the factor for E_A.

cules leaving the inner surface A_2 will have a velocity $\bar{c}_2 = \bar{c}_1 + a(\bar{c}_2' - \bar{c}_1)$ as before. Those leaving A_1, the outer surface, will, due to the large number of encounters, have $\bar{c}_1 = \bar{c}_1'$. Thus $\bar{c}_2 - \bar{c}_1 = a(\bar{c}_2' - \bar{c}_1')$. In this case $\bar{c}_2 + \bar{c}_1$ does not equal $\bar{c}_2' + \bar{c}_1'$. Actually, for small differences in temperature the difference is not great, so that one can write $\bar{c}_2^2 - \bar{c}_1^2 = a(\bar{c}_2'^2 - \bar{c}_1'^2)$. A rigorous analysis of the error due to this assumption with experimental verifications indicates that this holds quite well, and one can then assert that $\epsilon_{1\infty}$ for the concentric cylinders is given by $\epsilon_{1\infty} = a\epsilon$. Also one has that $\epsilon_{1\infty} = (2 - a)\epsilon_{11}$. Finally, Knudsen analyzes the case for two cylinders of dimensions which are the same order of magnitude. The resulting equations are more complicated. He finds an expression ϵ_{rR} which gives the heat conductivity in terms of ϵ, a, and a function of a, r, and R, the radii of the cylinders. By using the same inner cylinder, varying the outer cylinder and measuring ϵ_{rR}, he is able to get two equations giving a and ϵ.

The considerations above were put to experimental test by Knudsen. The details of the experiments, because of their extreme ingenuity, merit a description. They are, however, beyond the scope of the text. A few of the results may be cited.

For H_2 on glass, a was found to be $a = 0.26$. This used in the expression for ϵ_{rR} gives $\epsilon = 11.1 \times 10^{-6}$. The value of ϵ from the kinetic-theory calculation outlined above is 11.0×10^{-6}. This agreement is *fortuitously good* and is better than the experimental uncertainties warrant. It is possible, from the observed value of ϵ, to deduce the heat conduction for three different types of surface conditions in H_2 from the relations of ϵ_{11} and $\epsilon_{1\infty}$.

Absolutely Rough Surfaces in H_2	Glass and an Absolutely Rough Surface	Two Glass Surfaces
$\epsilon = 10.97 \times 10^{-6}$ cal.	$\epsilon = 2.9 \times 10^{-6}$ cal.	$\epsilon = 1.67 \times 10^{-6}$ cal.

Thus it is seen how much the value of ϵ is cut down by smooth surfaces.

Knudsen also measured a in H_2, using a fine wire and a concentric cylinder, thus obtaining $\epsilon_{1\infty}$. The results showed a to vary with the temperature. It took on the values 0.35, 0.376, 0.423 at 0, -79.5, and -192°C. This may simply mean that at lower temperatures the energy exchange with the surface is more nearly complete. Experiments with platinum and platinum-black sur-

faces in the three gases, H_2, O_2, and CO_2, gave the following table of values:

Pt	a =		
	H_2	O_2	CO_2
Polished	0.358	0.835	0.868
Slightly coated with black	0.556	0.927	0.945
Heavily coated with Pt black	0.712	0.956	0.975

In a much later paper Knudsen[62] returns to a study of the accommodation coefficient and especially the rôle played by translational and rotational energies in exchange. He carried out this investigation for the case of two thin platinum strips inside a large vessel. The arrangement corresponded theoretically to the case of a small wire in a large cylinder. One of the strips was polished platinum on both sides, the other one had a very rough surface on one side and a polished surface on the other. Measurements were carried out in H_2 and He. The equations used were based on the equation for energy transfer,

$$E = \sqrt{\frac{2}{\pi}}\left\{1 + \frac{3}{4}(k-1)\right\} p \frac{1}{\sqrt{\rho_0}} \frac{T_1 - T_2}{T_2},$$

which can be converted to

$$E = \frac{1}{2} p \bar{c}_0 \left\{1 + \frac{3}{4}(k-1)\right\} \frac{T_1 - T_2}{T_2} a$$

for the case of H_2 with the strip in a large volume and

$$E = \frac{1}{2} p \bar{c}_0 \frac{T_1 - T_2}{T_2} a$$

for the case of He. a is defined in this case as $a = \dfrac{T_0 - T_2}{T_1 - T_2}$, where T_0 is the temperature of the rebounding molecules, T_1 is the temperature of the strip, and T_2 that of the walls. As before $k - 1 = \dfrac{5/3 - \gamma}{\gamma - 1}$, where $\gamma = C_p/C_v$. If a'' is the value for the polished Pt, a' that for the rough surface, and if E'' is the energy transferred from the polished Pt, and E' that for the

rough Pt, one could measure T_1, T_2, p, and $E' + E''$ with the rough-smooth strip. With the smooth strip alone, E'' could be determined. These two measurements give $a' + a''$ and a'' in a monatomic gas (no rotation) and a bimolecular gas (rotation present). These measurements enable $a' - a''$ to be computed. Now, for only *translatory* (*i.e.*, momentum not energy) exchanges on impact, one has the accommodation coefficients a_t' and a_t'' for the rough and smooth surfaces. For a strip with one side rough and one side smooth, the differences in a_t must lead to a pressure difference on the two sides of the strip. Knudsen's experimental arrangements permitted this to be measured as $p' - p''$. The difference in pressure on the two sides of the strip is related to $a' - a''$ by $p' - p'' = \frac{p(T_1 - T_2)}{4T_2}(a_t' - a_t'')$ (see page 351). Since all quantities except $a_t' - a_t''$ can be evaluated in this equation, this measurement gives values for $a_t' - a_t''$ in a monatomic and a molecular gas. A comparison of $a' - a''$ in the case of energy exchange, and $a_t' - a_t''$ for momentum exchange, enables one to see at once whether for rotational motion in a gas a differs from a_t for translational. The results obtained gave:

For H_2

Conduction $a' = 0.735$, $a'' = 0.315$, $a' - a'' = 0.420$.
Radiometric forces gave $a_t' - a_t'' = 0.415$.

For He

Conduction $a' = 0.909$, $a'' = 0.411$, $a' - a'' = 0.498$.
Radiometric forces gave $a_t' - a_t'' = 0.512$.

This means that $a' - a'' = a_t' - a_t''$ whether rotation was present or not. Thus the experiments show that within the limits of error the accommodation coefficients for translatory energy and internal molecular energies are the same. The result indicates that the inner molecular energy is distributed independently of the translatory energy and that the Maxwellian distribution is applicable to both forms of energy. This conclusion justifies the mode of procedure used by Knudsen and removes the doubt cast by von Smoluchowski[17] on Knudsen's equation (see later).

The evaluation of a' and a'' enabled Knudsen furthermore to determine n'/n'', the approximate ratio of the number of

collisions which the molecules had in escaping from the rough surface compared with the smooth surface. It can be readily shown that this ratio is given by $n'/n'' = \log (1 - a')/\log (1 - a'')$. A similar relation was independently deduced and used by Roberts[67] in an important article to be discussed later. Knudsen found n'/n'' for He to be 4.5 and for H_2 to be 3.5. The difference probably lies in experimental inaccuracies which are very great when, as in He for rough surfaces, a approaches unity.

In a paper, M. von Smoluchowski[17] discusses the paper of Knudsen[16] and makes certain criticisms which are of value.* In 1890, von Smoluchowski[13] had experimentally tested the variation of K, the coefficient of heat conductivity, as a function of the pressure. He had found it to be independent of the pressure down to low values of the pressure. At the lower pressures he had observed departures from the predicted law. These he explained as being caused by the fact that the temperature drop at the surface of the wall was extending well into the conducting space at these pressures. The idea of this temperature drop, as has been said, came originally from the experiments of Kundt and Warburg on gaseous slip and was introduced by them. In two papers, von Smoluchowski[18] derived the theory of the temperature drop at surfaces, using two different viewpoints. In these deductions he also had to assume a lack of temperature equilibrium for molecules leaving the surface. His first theory assumed that molecules leaving a surface had a temperature Θ, while Θ_M was the average temperature of the molecules striking the surface and Θ_0 was the temperature of the surface. This led to the relation $\Theta_M - \Theta = (1 - \beta)(\Theta_M - \Theta_0)$. This relation is based on the same considerations as those used by Knudsen and leads to Knudsen's expression if $(1 - \beta)$ be replaced by Knudsen's a. The second theory depended on the same type of reasoning used by Maxwell for the coefficient of slip, that is, he assumed that a fraction f of the molecules was "absorbed" and reemitted and a fraction $1 - f$ was reflected. Under these assumptions the molecules in the fraction f have the temperature of the wall and the $1 - f$ are uninfluenced by the impact. As was discussed under the theory of the coefficient of slip, Baule[7] shows

* The paper of Smoluchowski[17] followed Knudsen's[16] first paper. The later paper of Knudsen[62] answers Smoluchowski's criticisms and by experiment shows them to be unjustified.

that f is capable of a more detailed analysis and definition in terms of the number of impacts necessary to bring it to equilibrium with the surface and the chance that it had these impacts. The equations deduced gave formally analogous expressions for the heat conduction, but ones which led to different numerical results for gases at higher pressures. In the conduction at lower pressures the theories are simpler, and it turns out that for plane parallel plates von Smoluchowski's first mode of approach gives $\epsilon_{11} = \frac{a}{2 - a}\epsilon$, in agreement with Knudsen's theory, and that for the latter theory $\epsilon_{11} = \frac{f}{2 - f}\epsilon$. This has the same form as Knudsen's expression for a, but its meaning is different. There is an essential difference between the two cases from a theoretical point of view. In Knudsen's theory, the directions of the emitted molecules are all random and the Maxwell distribution law holds for emitted molecules no matter what the distribution of impacting molecules. In the second theory for the $1 - f$ molecules reflected these may be reflected in special directions if the impacting molecules have certain chosen directions. Von Smoluchowski points out, however, that both Warburg's experiments on the slip of H_2 and Knudsen's experiments on thermal transpiration (Sec. 83) show f for H_2 to be near 1, while the experiments of von Smoluchowski interpreted in terms of his second equation show that f must be much less. Thus von Smoluchowski's observed f is not the same as the f which comes from slip, and this indicates that for the thermal exchanges the accommodation coefficient a must be used, while for momentum transfer another quantity f is used. In H_2, Knudsen found $a = 0.26$. It would seem, therefore, that the action of "surface roughness" is different for directional effects and temperature equilibrium on reflection, for it requires only one or two impacts of a molecule with the rough surface to wipe out all of its past history, while it takes many impacts for a molecule to reach thermal equilibrium with a surface.

In this connection von Smoluchowski points out that the calculation of E from E_T and E_A by Knudsen, in which the translational and rotational energies are treated as independent, is not justified. It is pointed out that it is likely that faster translational velocities will imply also faster rotations. Also it is pointed out that Knudsen's assumption that a is the same for

rotation as for translation is somewhat doubtful. Both are valid criticisms. The first one, however, raises the question of independence of velocity components in Maxwell's distribution law as deduced in Sec. 33. It seems probable that, as the speed is altered after each impact, the correlation feared by von Smoluchowski is not an important one. To correct this, von Smoluchowski gives an expression with three unknown coefficients a_1, a_2, and β, to multiply ϵ by in order to get ϵ_{11}. The a_1 and a_2 are presumably the accommodation coefficients for translational and rotational energies, and β is a constant between 0 and $\frac{1}{3}$. As a result of Knudsen's[62] later work these criticisms are unjustified and one may safely accept Knudsen's definition of the accommodation coefficient and his subsequent treatment as in essential accord with fact.

81. The Reflection of Molecules from Surfaces and Adsorption. *A. Statement of the Problem.*—The discussions involving Maxwell's slip term in the equation for the flow in tubes, and the accommodation coefficient in heat transfer problems, together with certain observations by Langmuir,[39,40,41] Chariton and Semenov,[45] and of Cockcroft,[63] Wertenstein,[64] and Clausing,[65] indicate that there is much that requires clarification in the fundamental interaction between molecules and solid surfaces. At the time of the writing of the first edition of this book, the issues were not at all clear. This was in part due to lack of sufficient experimental data which are now at hand and partly to the strong opinions expressed by workers, based on results obtained in experiments bearing on somewhat different aspects of the same phenomenon. Since that time the development of the technique of molecular beams has added very much important information so that the problem is somewhat clarified.[59] The development of the problem from the various viewpoints in 1926 has been adequately covered in the first edition of this book, and there is little but historical interest in a recapitulation of the views presented at that time. In what follows, only a brief review of this early aspect will be given, in order that space may be available for the treatment from the present-day point of view.

It will be recalled that the careful study of the slip term in the measurement of viscosity had shown that of the order of 99 per cent of the molecules of the gases (H_2, He, and O_2), studied by Blankenstein[8] were diffusely reflected from surfaces of

burnished silver oxide. This direct measurement of Maxwell's f thus showed it to be unity within the limits of experimental error in these cases. On the other hand, Knudsen observed values for the accommodation coefficient a for surfaces which indicated that, while the reflected molecules had in general a random distribution (indicating an interaction with the walls which wiped out their previous momenta), the *same molecules had not established temperature equilibrium with the surfaces struck.* While this difficulty received a logical explanation on the assumption that it took more impacts with a surface to establish thermal equilibrium than to give random directional emission, there were other results which confused the issue. These results came from the study of the deposition of molecular beams upon surfaces (*i.e.*, the condensation of molecular beams), the adsorption of gases on surfaces, and the "activation" and ionization of gases on impact with heated metal surfaces. Such studies convinced Langmuir,[39,40,41] the foremost early investigator in this field, that, in general, molecules "condense" on surfaces and reevaporate. In fact he extended his conclusions based on phenomena in which such action definitely took place to explain the diffuse reflection of molecules from surfaces in general. In addition, the results of Van Dyke[9,10] and of Millikan[49,51] on the coefficient of slip of air on surfaces of shellac, brass, and watch oil, the former using a rotating-cylinder method and the latter, oil-drop measurements, led to values of slip in which f was distinctly less than 0.99 as Blankenstein had observed it. Similar results on the diffraction of molecules from crystals also indicate the real existence of a type of specular reflection. Hence one has on one side the expressed view that *molecules condense on all solid surfaces and reevaporate* after a time τ which may be appreciable, such that diffuse emission on reevaporation and an accommodation coefficient of unity are to be expected (*i.e.*, $f = 1$, $a = 1$); and, on the other, that a is unity only for very rough surfaces, and that in some cases specular reflection of one type or another to the extent of 0.1 or more, $f = 0.9$, may occur. This definitely implies that τ is so short that a is less than unity, and in some cases no condensation occurs at all. It was pointed out in the first edition that a single *universal* picture could hardly be drawn for these phenomena, since such effects as condensation depended on the *forces* between surface and molecule, which for the diversity of substances used (*e.g.*,

metals on metals with which they amalgamated and inert gases on surfaces of metal or surfaces of occluded gas molecules) must vary over tremendous limits. Thus it was to be expected that diverse results would be found depending on the substances used and the surface temperatures and conditions. This has proved to be the case, as will be seen.

A priori one might, omitting the question of attractive surface forces entirely, study the structural effect of surfaces on the reflection of molecules of the classical type striking surfaces composed of molecules. Such a study, however, requires the assumption of spherical elastic solid molecules. It was in fact on these classical considerations that Maxwell and Smoluchowski worked. These considerations were carried to their logical conclusion by Baule. Baule reasoned that the fact that surfaces showed two constants of different values in interaction with molecules (*i.e.*, an a and an f) might be explained on the basis of *energy* and *momentum* exchanges of free gas molecules impacting on elastically bound spherical atoms or molecules in surfaces. Baule[7] assumed that a solid consisted of a cubic space lattice of elastic spherical molecules or atoms which vibrate about their equilibrium positions with an average kinetic energy corresponding to the temperature. The gas molecules strike these and rebound from them following the laws of elastic impact. Call E_1 the mean energy of the incident molecules, E_2 the mean energy of the molecules of the solid, and E' the mean energy of the gas molecules after one collision with the molecules of the solid. Then

$$E' = \beta E_1 + (1 - \beta)E_2.$$

In this equation β is given by the masses of the molecules and indicates the fraction of the energy of the incident molecules which they retain after one impact with the solid molecules. The value of β depends on the masses m_1 of the gas molecules and m_2 of the molecules of the solid, and is given by

$$\beta = \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2}.$$

Now some of the molecules make more than one impact before escaping from the meshes of the surface. For simplicity, Baule assumed that all those leaving after more than one impact have the energy E_2. Assume a fraction ν (this ν must depend on the

form of the surface) makes only one collision. Then if E is the energy of all molecules leaving the surface,

$$E = \nu E' + (1 - \nu)E_2$$

and thus

$$E = \beta\nu E_1 + (1 - \beta\nu)E_2.$$

Since the mean energy is proportional to their temperatures, it is possible to write

$$T = \beta\nu T_1 + (1 - \beta\nu)T_2,$$

or

$$(T - T_1) = (1 - \beta\nu)(T_2 - T_1),$$

which gives a, the accommodation coefficient of Knudsen as

$$a = (1 - \beta\nu).$$

Baule also calculated the value of the accommodation coefficient for viscosity. This is a quantity related to Maxwell's f. Call v_1 the average velocity component of the incident molecules parallel to the surface, and v_2 the tangential velocity of the surface in the same direction. Also let v' be the average velocity parallel to the surface of the molecules which rebound after one collision. Calling γ the constant of velocity exchange for one impact, he finds from analysis that γ depends on the masses of the molecules of gas m_1 and surface m_2 and is given by

$$\gamma = \frac{m_1}{m_1 + m_2}.$$

From this he deduces the relation

$$v' = \gamma v_1 + (1 - \gamma)v_2.$$

If, then, ν make only one impact and escape with the velocity v', while $1 - \nu$ are diffusely reflected, one has, if v be the average velocity component of *all* the molecules leaving the surface parallel to it,

$$v = \nu v' + (1 - \nu)v_2.$$

This at once gives

$$v = \gamma\nu v_1 + (1 - \gamma\nu)v_2$$

or

$$(v - v_1) = (1 - \gamma\nu)(v_2 - v_1).$$

In terms of Maxwell's theory, f is the fraction of the molecules absorbed and $1 - f$ is the fraction specularly reflected. The quantity $(v - v_1)$ in terms of Maxwell's f is then given by

$$v = v_2 f + v_1(1 - f)$$
$$(v - v_1) = f(v_2 - v_1),$$

and thus Maxwell's $f = (1 - \gamma\nu)$ in Baule's terminology.

The measurements of f and a help to evaluate ν and to check the theory.

For H_2 in contact with Pt, $m_1 = 2$, $m_2 = 195$, hence $\beta = 0.98$, and $\gamma = 0.01$. If the value of $a = 0.26$ be taken from Knudsen's experiments, then $\nu = 0.76$ and this gives $f = (1 - \gamma\nu) = 0.992$. This should be the accommodation coefficient for viscosity. This agrees well with experiment where the values found lie between 0.98 and 1.0. For Ar in contact with Pt, $m_1 = 40$, $m_2 = 195$, $a = 1 - \beta\nu = 0.85$ (Soddy and Berry), $\beta = 0.72$, $\gamma = 0.17$, and $1 - \gamma\nu = 0.965$. Thus f for gases should decrease with increasing density of the gases but is in any case near unity. Baule then analyzed the coefficient ν on various assumptions as to how the molecules on the surface are shadowed by others. Such assumptions must, perforce, be at best very hypothetical. Furthermore, Baule left out of account altogether the question of the action of surface forces. It is manifest that in many cases these are of prime importance, especially where the atoms condense on impact.

Zener[66] has attempted to account for the accommodation coefficient by considering impacts between gas atoms and surface atoms having a repulsive energy of the form $Ce^{-\frac{r}{d}}$ using the wave mechanics. The value obtained is

$$a = \pi^2\left(\frac{m_g}{m_s}\right)\chi\left(\frac{\Theta}{t}\right)\Omega\left(\frac{d}{\lambda}\right).$$

In this equation m_g and m_s are the masses of the atoms of gases and solids. The function $\chi(\Theta/t)$ represents the effect the quantization of the solid has on the value of a. λ is the de Broglie wave length of a gas atom having an energy kt. Θ is the characteristic temperature of the metal. The function $\chi(\Theta/t)$ can be computed and lies between $\chi(0) = 1$ and $\chi(\infty) = 0$. The function $\Omega(d/\lambda)$ is an integral which represents the effect of a finite time of collision in hindering energy exchange. It has the limiting values $\Omega(0) = 1$, $\Omega(\infty) = 0$. The ratio d/λ takes on more meaning if $\lambda = h/mv$ is substituted for λ. It becomes $\frac{d}{\lambda} = \frac{2d}{v}\left(\frac{mv^2}{2h}\right)$, so that $2d$ is the time the atom moves a distance twice that to change the energy to $\frac{1}{3}$ of its value. $mv^2/2h$

is the period of a linear oscillator whose energy levels are spaced by an amount equal to the kinetic energy of the atom. The only values with which to compare the theory are the values of a obtained for He on W by Roberts.[67] The temperature variation observed by Roberts agrees with Zener's theory, but the theory is unable to calculate the absolute values because of an unknown scale factor in Roberts' results, as well as in the theory which considers only normal incidence.

With the data discussed above it is clear that much remains yet to be done in a clarification of the theory of the accommodation coefficient. Many more complete experimental data are needed for various clean and soiled surfaces, as well as for other gases and metals. It is clear that the wave mechanics is pointing the way to a correct solution which is more likely to succeed since it enables one to introduce surface forces. Thus the very simple theory of Baule[7] is untenable as it does not envisage roughness and forces, while the wave-mechanical treatment is as yet too little developed. Hence a clarification of the issues raised can at present proceed only by a study of the experimental evidence to date.

In further discussing the problem resulting from conflicting data on specular reflection, accommodation, and condensation, one might approach it in attempting to answer certain questions. The first question raised is whether the f of Maxwell is ever less than unity, *i.e.*, whether real specular reflection occurs for molecules on surfaces. The second one, which can only be answered if the first is answered in the affirmative, concerns the condition under which specular reflection occurs and the reason therefor. The third question is whether every case of diffuse reflection must be ascribed to a temporary condensation and reevaporation. If this proves to be the case, one must then explain in terms of the time of lingering on the surface why it is that the accommodation coefficient is not unity in some of these cases. Another question of importance is the establishment by experimental investigation of a real condensation and reevaporation of molecules or atoms on surfaces, followed by a measurement of the time of lingering. If such a phenomenon is really proved to occur, then it becomes necessary to discuss the state of the condensed molecules on a surface. In the end it will be found that under certain circumstances a type of specular reflection of an unexpected nature does occur, and that condensation does occur, that under these

conditions the time of lingering varies between such very wide limits that it is possible to explain the difference between accommodation, reflection, and adsorption coefficients, and finally that these diverse behaviors must depend on the attractive force fields of the surfaces as regards the different molecular and atomic species used.

B. The Problem of Diffuse Reflection or Scattering.—This problem is discussed by Fraser[59] in his book on "Molecular Rays." Fraser introduces the problem by referring to the diffuse scattering of molecules by surfaces at low pressures without regard to equilibrium between surface temperature and gas, as the Knudsen law of molecular scattering. The reason for this appellation is that despite the fact that the scattering varies as the cosine of the angle, this law was first applied to non-equilibrium cases by Knudsen[68] in 1915, while the cosine law of surface scattering for a gas in temperature equilibrium with the surface was already in 1913 shown by Gaede[69] to be a consequence of the second law of thermodynamics. The *equilibrium* cosine law has also been derived independently by Epstein[70] and later by Clausing.[70] The equilibrium cosine law is valid for the most *general* kind of restitution, *i.e.*, scattering plus reflection, or for either type alone, while the Knudsen law applies to scattering alone and is of interest as it does not depend on conditions which mark specular reflection. The Knudsen law was first roughly tested by R. W. Wood[38] for Hg and Cd atoms on glass. Knudsen[68] established it more precisely for mercury.

The most accurate test of Knudsen's law was more recently made by Taylor,[71] using atoms of Li, K, and Cs, incident on the cleavage planes of NaCl and LiF crystals. The measurements extended from 2 to 60 deg. Using a surface ionization gage, he proved that in this case the Knudsen law was obeyed to 1 part in 10^4. This, according to Fraser, can only mean that in this case the atoms actually condense on these surfaces and later reevaporate. One sees therefore that in a particular case Knudsen's law is accurately obeyed. This also seems to be nearly the case for gas-coated and somewhat complicated surfaces such as those used by Wood,[38] Knudsen,[68] and Blankenstein.[8]

It was the suspicion of the author that the law might be attributable to the rough character of surfaces usually used and to the presence of foreign substances on the glass surface. At

the suggestion of the author and E. U. Condon, A. S. Adams in a master's dissertation early in 1926 scattered Zn atoms from the more regular cleavage plane of a crystal of MgO heated to about 200°C. The results obtained verified the cosine law and the thesis was never published. As is now known, the failure to obtain a different result was doubtless due to the use of a beam of Zn atoms which was not a true molecular beam. In 1928 Ellett and Olson[72] reported that Hg and Cd atoms reflected from the cleavage surface of an NaCl crystal heated in vacuum before use, gave a large percentage of specularly reflected atoms. A glass surface outgassed did not show this result. Na was not reflected, and H atoms were reflected as atomic H with no uniform results. A later,[73] more accurate study confirmed the preliminary results for Hg, Cd, and As on NaCl and also KCl, but neither fluorite nor orthoclase gave the result. A slotted-disc velocity analyzer showed these beams to have a nearly constant and narrow velocity range.[73]

The specularly reflected beam was found to be specularly reflected from a second crystal at the same angle of incidence. Cd atoms from an oven at 440°C. striking NaCl at 45 deg. gave a specular beam with 17 per cent of the incident atoms. An attempt to correlate this effect with a de Broglie wave length did not give a satisfactory agreement and there is no satisfactory theoretical interpretation at present. Almost simultaneously T. H. Johnson[74] found specular reflection of H atoms from rock salt. These experiments at first showed definite maxima corresponding to specular reflection. They were, however, complicated by an apparent roughness of the surface lattice and the fact that condensed atoms of H on NaCl (*i.e.*, those giving diffuse reflection) were reemitted as H atoms and were registered at the detector. In a later study, using H atoms on LiF, the reflecting power was found to be much greater (from 50 to 100 per cent at grazing incidence) and diffusely reflected atoms came off as molecules which were not counted by his MoO_3 detector. His technique enabled the complete diffraction pattern for H atoms in thermal equilibrium to be obtained. It proved quite completely the de Broglie wave character of the H atoms and confirms the work of Stern's group.

Probably the most striking and significant experiments indicating specular reflection are those of Knauer and Stern,[75] and Estermann and Stern.[75] These experiments were like Ellett

and Olson's and Johnson's experiments undertaken to verify the existence of the de Broglie waves associated with atoms and molecules of matter. The de Broglie equation ascribes to a body of mass m and velocity v a wave length λ given by $\lambda = h/mv$, where h is the Planck constant. Now for H_2 at room temperatures λ is of the order of 0.57×10^{-8} cm. The crossed-grating lattice of crystals of NaCl and LiF has a grating space such that waves of this length should be scattered at angles of 20 to 30 deg. which can easily be measured. At first without a velocity filter, and later with a velocity filter, Stern[75] and his collaborators succeeded in verifying the de Broglie equation to 1 per cent. Thus in this case not only is diffuse reflection absent, but the reflection is strictly governed by the laws of wave mechanics. These workers went further, for they investigated the reflection of H_2 from a polished surface of speculum metal. In this case the irregularities in the most highly polished surface are of the order of 10^{-5} cm. To make such a surface into one with irregularities of the order of 10^{-8} cm in order to look for specular reflection, the surface must be viewed at an angle θ of the order of 10^{-3}, *i.e.*, a few minutes of arc. At $\theta = 10^{-3}$ the reflecting power was 5 per cent, while at $\theta = 2 \times 10^{-3}$ it was only 1½ per cent. By reducing the temperature of their H_2 source to $-150°$C., Knauer and Stern found that the reflecting power for a crystal was increased 1.5 times. This is in excellent accord with theory, for in this fashion v is decreased and hence λ is increased in the ratio of $\sqrt{300/130} = 1.5$. Again the surface of a crystal is irregular because of the heat motions of its atoms. Thus the irregularities of the crystal can be reduced by cooling it, and as a result one would expect an increase in specular reflection for cooled crystal surfaces. This has been found to be true by Knauer and Stern, Estermann and Stern and by Johnson.

The problem of the reflection of atoms from crystals has been theoretically investigated by Zener[76] on the basis of the wave mechanics. The fraction of reflections for which all the normal coordinates of the crystal remain unaltered is given as approximately

$$U = e^{-3\pi^2}\left\{\frac{\left(\frac{m_A}{m_B}\right)\left(\frac{t_A}{\Theta}\right)^2\left(\frac{t_B}{\Theta}\right)}{\left(1+\frac{4\pi d}{\lambda}\right)}\right\}.$$

Here m_A and m_B are the masses of the reflected atom A and the crystal atoms B, Θ is the characteristic temperature of the lattice, d is the distance at which repulsive forces between atoms A and B fall to $1/e$ of their value, λ is the de Broglie wave length of the atom, kt_A is the energy of the atom A, and t_B is the temperature of the lattice. For A on Li at room temperature, U is about 0.9.

It is thus seen that in the study of specular reflection the latter must be regarded as a problem of the reflection or diffraction of matter waves from surfaces rather than from the particulate point of view. Under these conditions the reflection will be specular when surface roughness is reduced to the order of, or less than, the de Broglie wave length of the particles impinging on it. If the pattern is regular and of the right periodicity, regular diffraction of matter waves occurs, which is a specialized form of specular reflection. It must, however, be noticed that this occurs for H, H_2, and He on NaCl and LiF in an experimentally verifiable form, while for Ne, Ar, and CO_2 the effect was not pronounced, if present at all. What is perhaps an analogous effect, although it occurs at special large angles only and appears to be of a more classical nature, is the specular reflection of Hg, Cd, and As from NaCl and KCl. It is possible that Van Dyke's and Millikan's experiments giving a Maxwell's f on oil and mercury drops of the order of 0.9 can be explained by the specular reflection for grazing impacts. On the other hand, the experiments of Taylor show that for Li, K, and Cs on NaCl and LiF, *only diffuse* reflection occurs. This appears to be the case of Hg and Cd on glass and many other combinations where the Knudsen law is observed to hold. It is clear that the specular reflection can occur only in the absence of marked condensation on the surface, *i.e.*, where surface forces are weak.

Fraser suggests that the specular reflection is thus dependent on the critical data for the impinging gas. While this is doubtless a factor, especially for surfaces coated with layers of the gas in question, it need not be universally true. The attractive forces of the *surface* for the gas molecules or atoms in question must play a part and perhaps introduce new critical constants for the condition of the two-dimensional gas phase on the surface. Absence of strong surface forces must be the condition for the appearance of much specular reflection, while condensation must depend on strong forces. It is the importance of the nature

of the surface and the practical impossibility of learning anything about the character of the surface used that has caused much of the confusion.

C. The Accommodation Coefficient.—It is seen that the first two questions asked in the introduction have been answered, for it has been shown that, in addition to diffuse reflection, specular reflection also occurs, the conditions under which it occurs having been indicated. That condensation and reevaporation also occur was indicated by Taylor's results with Na atoms on rock salt. Since both these phenomena occur, the nature of their influence on the accommodation coefficient must next be determined. Some important information is yielded in this direction by the experiments of Roberts.[67] Roberts studied the accommodation coefficients for fine W and Ni wires, using He gas. He utilized for the analysis of his data Knudsen's[62] equations for the case of a fine wire in a large cylinder (see Sec. 80). He worked, however, with outgassed surfaces, in very pure He, the metal being denuded of surface films of gases by flashing at a high temperature. In this way he was able to study a as a function of the gas adsorption on the surface, both for a relatively smooth wire and for a roughened one. If T_0 is the temperature of the molecules coming from the gas (*i.e.*, the cold cylinder walls), T_2 is the temperature of the wire, and T_2', T_2'', . . . , T_2^n is the temperature of the molecule rebounding from the wire after 1, 2, . . . , n collisions with it, then

$$\begin{aligned} T_2' - T_0 &= a(T_2 - T_0), \\ T_2'' - T_0 &= a(T_2 - T_2'), \\ T_2^n - T_2^{(n-1)} &= a(T_2 - T_2^{(n-1)}). \end{aligned}$$

If one call a_n the accommodation coefficient observed for a molecule that has rebounded n times with the surface T_2 before escaping, one has

$$T_2^n - T_0 = a_n(T_2 - T_0) \text{ by definition of } a_n,$$

whence

$$a_n = 1 - (1 - a^n).$$

This is the equation used by Knudsen for the measurement of n. If one knows the value of a, and computes the values of a_n for $n = 1, 2, 3$, etc., then for an observed a_n one can estimate

roughly the relative numbers of molecules that have made one and two, two and three, impacts with the surface. Roberts observed for He on W the following values:
Measured a:

Clean Surface	Dirty Surface
0.07	0.19
0.12	0.40
0.18	0.55

The values of a for the smooth surface increase from 0.07 to 0.18 on prolonged heating of the wire, which increases surface roughness. A clean wire that is heated only briefly gives the values of 0.07; and, if dirty, of 0.19. If the changes in the clean-surface values are due to increased roughness, it can be shown that the clean-surface value 0.12 corresponds to a_n due to molecules for which $^7/_{13}$ have $n = 2$, and $^6/_{13}$ have a value of $n = 3$. If these values are used, then the computed values for a clean and dirty smooth surface are 0.05 and 0.19. The value of 0.55 for a rough dirty surface indicates that $^1/_5$ of the molecules escape with $n = 3$ and $^4/_5$ with $n = 4$. These values enable one to calculate a for smooth clean and dirty surfaces of 0.05 and 0.18. Thus these values for n enable one to interpret the results in terms of a about 0.05 for a clean smooth surface and 0.19 for a dirty one. The supposedly clean and smooth surfaces were not absolutely smooth, but, according to Roberts, they set an upper limit which is not off by more than a factor of 2. The values for Ni were 0.085 clean and 0.20 after standing. As the values for the dirty surfaces should be independent of Ni and W, the value 0.20 for the dirty surface is practically constant. The value for clean Ni is, however, 0.08 relative to a value between 0.05 and 0.07 for W. Roberts then points out that specularly reflected atoms do not contribute to the energy exchange. He therefore attempts to explain the value of a observed, assuming that those molecules diffusely reflected leave in temperature equilibrium with the surface. This identifies a with what is here termed Maxwell's f. (See page 323, where Smoluchowski makes the same assumptions.) Actually the f observed is usually nearly 1 while a is distinctly less than 1, and Roberts theory is incorrect. Roberts also tests Baule's theory for the value of a in the case of He on Ni and W. Since the mass ratios enter into a on this theory, calculation shows that a for He on Ni is about twice the value experimentally observed.

Thus Baule's theory is inadequate, as was to be expected as it ignores too many structural features. In a later paper Roberts shows that for He on W the value of a decreases with temperature. It is 0.057 at 295° abs. and 0.047 at 190° abs. and 0.025 at 79° abs. It may be 0 at 0° abs.

Aside from the information gained about the effect of adsorbed gas layers and the values of n, the paper brings out an important point. It indicates that in one of those cases where much specular reflection might be found, *i.e.*, He on a clean metal surface, the value of a is surprisingly low. This makes it clear that, if one wishes to understand what occurs at surfaces, measurements of f, a, and perhaps adsorption should be made on the same surface under comparable conditions. Since a and f must be related in some fashion, it is only by such studies that these conditions can really be understood.

For the case where values of a are found that are less than the values of Maxwell's f, it must mean that either (1) it takes fewer collisions to wipe out a previous momentum than it does to alter the energy, or (2) the time of lingering on condensation is great enough in such cases to alter the directional velocity distribution but not great enough to alter the energy values by the full amount found for equilibrium. In general it would be easier from a classical mechanical point of view to consider that diffuse reflection can take place *without condensation* and reevaporation (*i.e.*, as might be the case for slight surface roughness) and explain the differences and values of a and f in terms of the number of impacts to gain equilibrium. This is doubtless the correct interpretation, for, as will be seen, in some cases the actual time of lingering becomes comparable with the time of an elastic impact.

D. The Adsorption of Molecules.—In the problem of adsorption on surfaces the situation is almost as complex and the experimental data fully as incomplete and unsatisfactory as in the case of f and a, owing to the difficulty of working with clean and known surfaces. In one sense the problem is simpler, inasmuch as one is dealing with a question which permits of classical approach in that condensed molecules on a surface may be treated as a sort of two-dimensional liquid in interaction with its vapor. Such a viewpoint enables one to overlook much of the doubtful mechanical picture and to deal with energy relations of which one can be reasonably sure.

The question of condensation on surfaces in the case of molecular beams was first raised by R. W. Wood[38] in what he called *diffuse reflection* of atoms from walls. Shortly after Wood's work, Knudsen[68] also published a paper on this subject. Then followed a series of researches by Langmuir[39,40,41] on adsorption which connected diffuse reflection with adsorption. Langmuir thus extended the theory of adsorption to cover diffuse reflection. In this generalization Langmuir doubtless went further than he was justified in doing, in asserting that all diffuse reflection was due to a condensation and reevaporation process, and that molecules all condensed for some average time τ on the surface, thereupon reevaporating. In making this claim, Langmuir was actually focusing attention on a series of phenomena where the condensation was important and did occur. Actually, as Clausing[65] shows in his paper, Langmuir recognized the possibility of specular reflection and of random scattering on reflection without condensation. Langmuir, however, focused attention on the condensation phenomena and did not consider the cases he mentioned. From what has gone before on specular reflection and in the case of diffuse reflection from the values of the accommodation coefficient, it is clear that true condensation for an appreciable average time τ on a surface does not occur in all cases. If τ exceeded several molecular vibrations, which occur in a solid in about 10^{-12} sec., there would be no specular reflection and the accommodation coefficient would be unity. If the heat of condensation is considerable, *i.e.*, if there are surface forces on the molecules of a gas such that the energy of agitation at a given temperature is of the order of the potential energy of the condensed molecules, larger values of τ can be expected. If the heat of condensation is somewhat less than the energy of agitation there will be some condensation, but the average life on the surface τ (time of lingering) will be quite short. As varying conditions of gas pressure, temperature, surface covering, and gas species used can extend the relative energies of agitation and condensation over an enormous range, one may expect τ to vary from values equal to the time of an elastic impact with the surface to a time involving perhaps hours, corresponding to a stable condensed film. As regards the smaller values of τ, enough has been said in what has gone before, for the values of f and a observed indicate their existence. One is now interested

in the evaluation of τ and in relating it to the energies of condensation and the behavior of adsorbed surface layers.

Following the theory that Langmuir developed as a result of his studies, others carried the work farther. Wertenstein[64] in 1923 measured τ for mercury atoms on glass and evolved a theory. In 1924 Frenkel[43] developed a theory of the phenomenon differing in some important details from Langmuir's. Langmuir had assumed that the forces of adsorption were localized at certain active regions of the surface lattice and had developed his theory from this point of view. There is evidence that on clean outgassed metal surfaces the condensation may be governed by such considerations. Frenkel studied the condensation, assuming that the condensed molecules formed a mobile sort of two-dimensional gas phase on the surface. In the cases where surface forces were not great, τ would not be expected to be large and no condensate could form under ordinary circumstances. If, however, the beam was so dense that with the mobility on the surface one or more atoms on the surface could unite to form molecules or agglomerations which did not so readily evaporate (*i.e.*, for which the time of lingering, τ', was greater) before the atoms evaporated, a monomolecular layer could form and be stable. This theory was treated in detail in the first edition of this book. Both Langmuir's theory and Frenkel's theory lead to the expectation that the question of the formation of a deposit at a given temperature must depend on the density of the impinging molecular or atomic beam. This expectation was in part substantiated by a beautifully simple experiment of Chariton and Semenov.[45] Volmer and Estermann,[77] Volmer, and others indicated that the assumption of the motion of the molecules over the solid surface actually took place as postulated by Frenkel in cases investigated by them. In these cases the surface was probably covered with a monomolecular gas film on which the metal atoms moved. In 1926 Cockcroft,[63] in a splendid series of experiments, verified the findings of Chariton and Semenov and of Volmer and Estermann and established Frenkel's theory in a semi-quantitative fashion. In 1928 Hückel, in his book on adsorption, treated the problem exhaustively from a thermodynamical point of view, using the concept of a two-dimensional gas. Finally a series of very exhaustive studies by Clausing,[65] both experimental and theoretical, have appeared in which direct measure-

ments of the time of adsorption on clean outgassed surfaces were made for certain gases in such a fashion that Frenkel's mechanism did not come into play. While definite results were obtained, they again indicate the technical complexity of an experimental study and the inability to generalize. Each result depends on the circumstances attending it and gives information as to what has happened in that case but does not lead to a general picture. The theoretical situation is the same as that found in the study of the real gas laws, there being in reality no single and complete law as more suitable data appear, but in reality a special law for each type of gas. In the present case the variations in behavior are in the first-order terms, but are more difficult to study, in that the results are harder to obtain and their significance is more doubtful in view of the impossibility of controlling surface conditions.

In this edition of the book Frenkel's derivation will not be given. The theory will be developed in a preliminary fashion following the more rigorous discussion of Clausing, and the two theories, that of Langmuir and that of Frenkel, will be given in the form of the final equations only, their merits being discussed in the light of experiment.

The discussion as to the nature of the average time spent on the surface (time of adsorption or time of lingering) must begin with the well-known law that the number of molecules ν striking a cm^2 of surface per second is $\nu = nu/4$, where u is the average velocity, not necessarily the $\bar{c}$ of Maxwell's law. This law, according to Clausing, is *independent of the distribution of velocities and of intermolecular impacts* but does *require the cosine law of scattering or emission* from the surface. Consider an enclosed volume V with a surface S exposed to the gas, then one can write an equation

$$\frac{1}{4}nuS\lambda = Vnu$$

in which λ is a quantity which defines the average path length of the molecules in the gas space between collisions with the wall. This follows since Vnu is the total distance covered by all the molecules in V per second, while $nuS/4$ is the total number of impacts on the walls of these same molecules; thus $\lambda = Vnu/(\frac{1}{4}nuS)$, *i.e.*, a sort of free path. The equation may be written

$$S\frac{1}{4}nu\frac{\lambda}{u} = Vn.$$

Here the quantity $\sigma = \lambda/u$ represents the time which the molecules leaving the walls consume on the average between successive collisions with the walls. Hence $Snu\sigma/4 = Vn$ represents the total time per second which the molecules spend in the container. The equations above simplify to $\lambda = 4V/S$ which is precisely the equation deduced on page 42 originally due to Clausius and depends on the cosine law but not the distribution law. In studies of absorption, λ should be made as small as possible, which can also mean that $\sigma = \frac{4}{u}\frac{V}{S}$ should be as small as possible. This means that not only must σ be small, but it must be small compared to the time τ_e which is the average time that the molecules linger on the surface. The ratio between σ and τ_e in equilibrium is obviously proportional to the ratio between Vn, the number of molecules in the gas phase, and aS, the number adsorbed on the surface, a representing the number of adsorbed molecules per cm^2 of surface, hence

$$\frac{\sigma}{\tau_e} = \frac{Vn}{Sa}.$$

Since $\sigma = \frac{4}{u}\frac{V}{s}$,

$$\frac{4V}{uS\tau_e} = \frac{Vn}{Sa}, \text{ and } \nu = \frac{1}{4}un,$$

whence

$$a = \nu\tau_e.$$

This very simple relation represents a very important law. It shows that in a wall bombarded by ν molecules per cm^2 per second, a, the number per cm^2 on the wall at any time, is given by $\nu\tau_e$ where τ_e represents the average time of lingering or sojourn in the adsorbed state. It is interesting to note that this gives a very broad definition of adsorption such that, if τ_e is of the order of 10^{-13} sec., specularly reflected molecules are adsorbed in this sense. This broad conception will be utilized hereafter, and it is clear that it does not in this regard conflict with data on a and f.

This law is independent of pressure, nature of impacts among the molecules in the gas phase, and of the distribution law. It does depend on the assumption of the cosine law of emission

from the surface and on the assumption that the velocity distribution of molecules leaving the surface is isotropic in space. Both of these assumptions are required to maintain consistency with the second law of thermodynamics. The law is particularly important, as it shows that the cosine law as an equilibrium law inevitably leads to an average time of lingering on the surface, though this time may be very short and of the order of the time of elastic impact. Whether this law can be extended to non-equilibrium cosine distribution, *i.e.*, the Knudsen law of Fraser is not certain as the deduction given covers equilibrium only. It is clear that it cannot extend to specular reflection. Thus specular reflection, where it occurs, excludes even this broad interpretation of condensation. Hence it is seen that irrespective of hypotheses peculiar to any special theory, there is a *true average time of lingering for any surface in equilibrium*, although the number of molecules on a unit area of surface, a, may be complicated by the fact that a is a function of the density of molecules on the surface (*e.g.*, as in Frenkel's theory). Thus the problem involved in a study of adsorption is that of ascertaining the relations between a and $\nu\tau_e$ for different cases. There is, of course, the possibility of conducting experiments so that molecules on the surface do not interact with each other (*i.e.*, in which a is so small that molecules never get near enough to influence each other). In this case the relationship between a, ν, and τ_e is exceptionally simple, and, if a and ν can be evaluated, τ_e can be measured. This Clausing later does by a direct but complicated investigation.

The fact that an adsorption time is defined as above leads to a study of other times of adsorption which have been assumed. Consider a surface which has adsorbed a molecules per cm^2 and is in statistical equilibrium with the gas space. In the time dt, νdt molecules strike the surface and of these one may assume that the fraction ρ are specularly reflected. By specular reflection is meant all emission of individual molecules in which the characteristics of emergence are determined by the characteristics of impact. All other emission is called diffuse, whether it is a reflection or an adsorption and subsequent emission. Thus the ρ here used is in reality Maxwell's $(1 - f)$. Hence the number of molecules adsorbed in a time dt will be $(1 - \rho)\nu dt = b_0$. It can be imagined as possible, starting at a time $t = 0$, to tag all the molecules that are incident in an interval dt. By means

of such tags the molecules can then be identified, and one could determine b, the number left at any time, t, later. If one call wdt the probability that a molecule will leave the surface in a time element dt, then

$$db = -bwdt,$$

and if w is independent of t, one has at once that

$$b = b_0 e^{-wt}.$$

If one call τ the average time during which the b_0 molecules remain on the wall after impact, one has

$$\tau = \frac{1}{b_0}\int_{b_0}^{0} -tdb = \frac{1}{w}.$$

Thus w is the reciprocal of the average time τ on the surface. Previously τ_e was defined as $a = \nu\tau_e$, and, if reflection occurs, the number incident per second is not ν but $(1 - \rho)\nu$. Since the average life of a molecule on the surface is τ as deduced above, one must write that $a = \nu\tau_e = (1 - \rho)\nu\tau$, so that $\tau_e = (1 - \rho)\tau$. Actually τ_e is inferred from a, so that the real time of sojourn is $\tau = \tau_e(1 - \rho)$.

According to Clausing these generalizations hold if the molecules influence one another on the surface, as dt is chosen so small that the effect may be considered negligible since b_0 is infinitesimal. It is, however, essential that all adsorbed molecules be identical since otherwise there would be different values of w for each kind. In practice either on Langmuir's theory of certain special privileged positions on the lattice or on Frenkel's theory of greater τ for agglomerated molecules, this is not the case, and it is probable that the conditions in reality are more complex than the simple considerations envisage. Langmuir's approach in the study of the subject differed from that of Knudsen and Wood. The latter assumed that a critical temperature T_n for condensation for a substance A on a surface B existed. If T, the temperature of A, was greater than T_n, according to them, condensation could not occur; while if $T < T_n$, condensation occurred. Langmuir assumed that condensation occurred for all substances, even though only for a short time. If the view of Knudsen and Wood were correct, the number of molecules striking the surface, and those reflected, would be equal until the critical temperature T_n is reached. On Langmuir's theory

of condensation and reevaporation, the incoming molecules are not directly related in number to the evaporating molecules, which are governed by the temperature of the surface and the chance of reevaporation. Under these circumstances, it is conceivable that at $T > T_n$, ν can become so great that condensation will occur despite this fact. This view, that condensation depends on the density of the impinging molecules and that T_n is a function of this quantity, has now been established beyond question by the experiments of Chariton and Semenov,[45] Estermann,[77] and Cockcroft.[63] Langmuir later studied the isotherms for the adsorption of the permanent gases on Pt, glass, and mica. The results lead to an equation for condensation on glass and mica identical in form with one deduced by Hückel which will later be given. To this theory Langmuir added the idea that it was only at certain points, i per cm^2 in number, in the lattice that molecules could be adsorbed. If a molecule strikes a point at which adsorption is impossible, it is reflected. If it strikes one of the i points which is unoccupied, it has a chance α of being adsorbed and $1 - \alpha$ of being reflected. Actually Langmuir sets α as equal to unity. Hence the coefficient of reflection is composed of two parts. Call ζ the fraction of cells occupied in the stationary state. Then $\rho = \zeta + (1 - \alpha)(1 - \zeta)$. Since $\zeta = a/i$, one has $\tau_e = \left(1 - \frac{a}{i}\right)\alpha\tau$ and $a = \nu\left(1 - \frac{a}{i}\right)\alpha\tau$, so that $a = \nu\alpha\tau i/(\nu\alpha\tau + i)$. If ν is small then $a = .\nu\alpha\tau$, and if ν is large the layer becomes monomolecular, *i.e.*, $a = i$. The time $\alpha\tau$ is the average time of adsorption of molecules falling on a clean surface. The value of $\alpha\tau$ for various gases and surfaces has been determined by Langmuir and is summarized in Clausing's article. The values range from 10^{-6} to 10^{-4}. The results, contrary to expectation, show i to depend on temperature, which is not consistent with the concept of i. Thus, while in detail the theory of Langmuir is wanting, the values of $\alpha\tau$ inferred probably correctly represent the order of magnitude of the time of adsorption, since, as ν decreases, the ideal conditions defining τ are more and more nearly given by the fundamental relation $a = \nu\alpha\tau$.

From the laws of statistical mechanics, Jaquet[78] and Hückel[78] have shown that τ_e is given by an expression of the form:

$$\tau_e = \frac{C}{\sqrt{T}} e^{-\frac{\phi}{kT}} = \frac{C}{\sqrt{T}} e^{-\frac{\Phi}{RT}} = \frac{C}{\sqrt{T}} e^{\frac{u}{RT}}.$$

Here C is a constant; T is the absolute temperature; τ_e is the average time of adsorption in seconds; $k = R/N_A$, where R is the gas constant per mole; and N_A the Avogadro number, ϕ is the energy of an adsorbed molecule which in general is less than 0, $\Phi = N_A\phi$, and $u = -\Phi$, the heat of adsorption per mole. For N_2 on mica, Langmuir sets $i = 1.79 \times 10^{14}$, $C = 1.22 \times 10^{-7}$ and $u = 1{,}500$. Wertenstein[64] found for Hg on glass the value of τ_e at 21°C. to be 1.08×10^{-5} sec. Frenkel, from statistical reasoning,[43] obtains the relation that

$$\tau_e = \tau_0 e^{-\frac{\phi}{kT}} = \tau_0 e^{\frac{u}{RT}},$$

where τ_0 is the period of oscillation of the surface molecules of the lattice surface. There is only one essential difference between Frenkel's equation and that of Langmuir and Hückel beyond the value of the constants of the factor multiplying the exponential, and that is that this factor in Frenkel's theory is *independent* of T, while, on Hückel's theory, it varies as $1/\sqrt{T}$. Cockcroft has tested Frenkel's theory for Cd on Cu between -90 and -150°C. and finds it to hold satisfactorily, giving a value of $u_1 = u_0 + \Delta u_1$ of 5,680 cal. per mole. Here u_0 is the heat of adsorption of a single Cd atom on Cu, and Δu_1 is the energy of dissociation for a pair of Cd atoms on the surface. At -100°C., τ_1 was found equal to 3.4×10^{-2} sec., where τ_1 is somewhat different from τ_e, depending on the formation of pairs. Cockcroft finds, however, that this does not establish Frenkel's theory that the *paired* atom is the stabilizing feature, since any grouping of atoms would give an analogous result but with different constants. From the small value of the heat of adsorption of 5,680 cal., compared with the heat of sublimation of Cd, which is 32,000 cal., Cockcroft concludes that smaller aggregates may play a rôle rather than larger ones. There may of course be no formation of pairs involved at all in this case, u_1 being sensibly equal to u_0. The range of temperatures studied is too small to give any decision between the Frenkel and the Langmuir-Hückel theories. Cockcroft further shows that the outgassed surfaces give far better condensation, as is to be expected, and it was clearly shown that u_1 for Cd on a pure outgassed Ag

surface was distinctly greater than for a gas-coated Cu surface. The effect of surface contamination on the values of u_1 was also shown by Cockcroft for the case of the condensation of Cd on Cu at different temperatures.

A direct attempt at the measurement of τ_e was made by Clausing[76] on a suggestion by Holst. A vertical molecular beam struck a rapidly rotating horizontal plate. The molecules of this beam were adsorbed on the plate and carried along in the direction of rotation and reemitted to a cooled surface. The horizontal displacement of the condensate from the point of impact could then be measured. From the speed of rotation it should be possible to infer the average time of adsorption. Clausing used Cd vapor on glass, picein (a wax), mica, and copper. Owing to the momentum imparted to the molecules by the disc on emission, there was a displacement of the beam. This displacement masked any adsorption time of less than 10^{-6} sec., as the momentum imparted caused a displacement of the same order of magnitude. Thus, at 200°K, Clausing was only able to state that for all these surfaces τ_e was less than 10^{-6} sec. Clausing also calculated τ_e for some data given by Becker[80] for alkali atoms on oxidized and clean surfaces of W. Becker finds a to correspond to a monomolecular layer or in some cases a thicker layer. For layers where a is that for a monomolecular layer τ_e is not 0 and the values of τ_e between 700 and 910°K range from about 600 to 18 sec.

Clausing[65] then devised and carried out a most ingenious but difficult measurement of the time of adsorption of various gases, A, Ne, and N_2, on clean glass surfaces. The method was to admit the gases suddenly to perfectly clean outgassed capillary-tube surfaces at such low pressures that interactions between adsorbed atoms on the surface could not occur. From the theory of the flow of gases through tubes at low pressures, the effect of the time of adsorption on the flow can be computed and compared to the flow under equilibrium conditions, when as many molecules reevaporate as condense. These measurements enabled him, as a result of a theory for which there is no space in this text, to evaluate τ_e and to find the law of adsorption. The study consists of measuring the increase in pressure with time in a vessel as a result of the flow from another vessel at a very low pressure of the gas through a clean outgassed capillary tube. The curve of pressure variation permits of the evaluation

of $\bar{t}$, the average time required for a molecule to traverse the capillary. $\bar{t}$ is related to τ_e by the equation

$$\tau_e = 2\left(\frac{2r}{L}\right)^2 \bar{t} - \frac{2r}{u},$$

where r is the radius of the tube, L its length, and u is the average molecular velocity. With A and N_2 the results were not reproducible despite the greatest pains to get uniformly clean surfaces. A final technique, which was believed to be without serious defects, enabled the temperature variation of τ_e to be measured. For A on glass between 78 and 98°K, he obtained

$$\tau_e \sim 1.7 \times 10^{-14} e^{\frac{3,800}{RT}}$$

with τ_e at 78° about 75×10^{-5} sec. and at 90° about 3.1×10^{-5} sec. For N_2 no results are reported, and for Ne on glass at 78 and 90°K τ_e was less than 10^{-7} sec. Using a modification which enabled a wire of W to be used in the tube, preliminary results showed that A on W had a value of τ_e about 1,000 times as great as on glass. The movement of the adsorbed molecules over the surface of the glass did not influence these measurements.

The theory of the flow through capillary tubes for the case where τ_e is so short that it does not influence the flow gives the average time $\bar{t}$ for a molecule to get through the tube as $\bar{t} = L^2/4ru$, where L is the length, r the radius, and u the velocity of the molecules. This law holds only for gas pressures so low that molecules do not collide with each other, and if the cosine law of diffuse scattering holds. In these experiments A and Ne were used with glass tubes at such a temperature that τ_e was negligible. The temperatures were room temperatures which gave an estimated τ_e for A on glass of 10^{-11} sec. The average velocity u, derived from the observed flow, lay within the limit of error of 2 per cent in respect to that calculated from the Maxwell distribution law. Thus Clausing believes that he has tested the distribution and the cosine law of reflection simultaneously to a high degree of precision. This verification of Maxwell's law is interesting but is of the same type as that given by Knudsen from effusion (see Sec. 79).

Thus it is clear from the discussion which has preceded that in general the interaction of molecules with surfaces represents

a very widely differing range of manifestations, which is particularly sensitive to surface conditions, nature of gases and surfaces, and temperatures. Definite evidence exists for some types of specular reflection. In other cases there is diffuse reflection without temperature equilibrium with the surface, with τ_e so short that it can be set equal to the time of impact. Finally in many cases there is an actual time of sojourn, τ_e, of atoms or molecules on surfaces in the form of an adsorbed layer which may vary from 10^{-11} sec. to hundreds of seconds. It also appears that in some cases the molecules are free to move or creep over the surface and that the formation of groups influences the adsorption by prolonging τ_e. In other cases it is probable that molecules or atoms are adsorbed at certain points in the surface lattice and this presents a complicating influence in that it gives multiple values of τ_e for the same atoms for different points on the surface. Real progress in this field is, however, exceedingly difficult because of its complexity and because of the practical impossibility of knowing the nature of the surfaces worked with. One must finally conclude that no one of the various generalizations made in the early days of study are universally applicable, though most of them are correctly conceived to explain the situations from which they were inferred. Thus again one sees the futility of emphatic generalizations in the absence of adequate experimental data.

82. The Absolute Manometer.[14]—The considerations thus far dealt with have shown that for very low pressures where the distance covered by the molecules is large compared with the distance between surfaces, conditions arise that somewhat simplify the kinetic-theory treatment of the phenomena. In the preceding sections the flow of gases through tubes has been investigated as well as the transport of heat from one surface to another. The former phenomenon at the low pressures gave the volume of gas flowing through per unit-pressure difference as independent of pressure. The heat conduction between parallel plates at the low pressures was, however, proportional to the pressure. It might be asked how the momentum transfer *normal* to the surfaces varies with the pressure of the gas. Investigation will show that it is proportional to the pressure. If this momentum transfer could be accurately measured in terms of mechanical force, it is possible that this would be a method of accurately measuring

low pressures. This, in fact, Knudsen has achieved, and it is of interest to give here the theory of the absolute manometer of Knudsen.

To study momentum transfer, Knudsen makes use of the fact that the molecules leaving a heated surface have a higher velocity than those leaving a cool surface. Thus there will be a force between the two surfaces, and this can be measured by a sensitive balance.

Such forces have been in the past called radiometric forces, as they were then identified with the forces acting in the Crookes radiometer. In the latter instrument vanes blackened on one side, suspended in an evacuated chamber, were shown to have forces exerted on them when illuminated with radiant energy on the blackened side. Concerning the theory of such radiometers more will be said later. Here it may be mentioned that these phenomena are differentiated from the Knudsen case because they take place at much higher pressures, that is, well above 0.001-mm pressure. The effect at the higher pressures turns out to be, in reality, an edge effect, as long before postulated by Maxwell,[19] and not a surface effect, as in Knudsen's case.

Assume two plates A_1 and A_2 of different temperatures. It is also to be assumed that their area is large compared to the distance between them, which is, in turn, small compared with the mean free path of the molecules (*i.e.*, less than one-tenth the mean free path). It is assumed that A_1 has a higher temperature than A_2, and that hence the molecules leaving A_1 have a velocity $\bar{c}_1$ greater than $\bar{c}_2$, that of the molecules leaving A_2. Assume that there are N_1 molecules per cm^3 of velocity components directed towards A_2 from A_1, whose average value is $\bar{c}_1$ and whose average squared value is $\overline{G}_1^2$. Similarly, assume there are N_2 molecules per cm^3 leaving A_2 with velocity components towards A_1 of average velocity $\bar{c}_2$ and of average squared velocity $\overline{G}_2^2$. It is then possible to get the number striking the surfaces per unit time and hence the momentum transfer per second, or the force per unit area. If one had considered the molecules which had velocity $\bar{c}_1$ components towards A_1 as well as away from it in an equilibrium case with A_2 absent, the number would have been $2N_1$ and the pressure would have been given by $\frac{2}{3}N_1 m\overline{G}_1^2$. Now the pressure on A_2 is caused by only the mole-

cules moving towards A_2, hence the pressure due to these molecules on A_2 is $\frac{1}{3}N_1m\overline{G}_1^2$, the molecules losing their energy on striking the surface. On the other hand, by similar reasoning, A_1 receives $\frac{1}{3}N_2m\overline{G}_2^2$ from the molecules leaving A_2 and striking A_1 with a velocity $\bar{c}_2$. The net momentum transfer to the two surfaces per cm^2 per second, and hence the force between them, will be the sum of these two, and thus K', the pressure between the plates, is $K' = \frac{1}{3}m(N_1\overline{G}_1^2 + N_2\overline{G}_2^2)$. As was shown in Sec. 80, the quantities $N_1\bar{c}_1$ and $N_2\bar{c}_2$ must be related by the expression $N_1\bar{c}_1 = N_2\bar{c}_2$ when equilibrium exists. Again, if the number of molecules outside the plates and their average velocity are designated by $N\bar{c}$ then, as was shown in Sec. 80, $N_1\bar{c}_1 = N_2\bar{c}_2 = \frac{1}{2}N\bar{c}$. Outside the plates the pressure is $p = \frac{1}{3}Nm\overline{G}^2$. The force outside per cm^2 is then the pressure outside, which is p, and the resulting force K acting on the plates per cm^2, that is, the force measured, is $K' - p$. This gives at once that

$$K = K' - p = p\left(\frac{K'}{p} - 1\right),$$

and substituting for p and K',

$$K = p\left[\frac{N_1\overline{G}_1^2 + N_2\overline{G}_2^2}{N\overline{G}^2} - 1\right].$$

Using the relation between $N_1\bar{c}_1$, $N_2\bar{c}_2$, and $N\bar{c}$,

$$K = p\left(\frac{\frac{1}{2}\left(\frac{\overline{G}_1^2}{\bar{c}_1} + \frac{\overline{G}_2^2}{\bar{c}_2}\right)}{\frac{G^2}{\bar{c}}} - 1\right).$$

Now $\overline{G}/\bar{c} = \sqrt{3\pi/8}$ (see Sec. 35), and the question arises whether this relation also holds for $\overline{G}_1/\bar{c}_1$ and $\overline{G}_2/\bar{c}_2$. Where the difference of $\bar{c}_1$ and $\bar{c}_2$ is small this can be assumed to hold. Hence one may write $\overline{G}/\bar{c} = \overline{G}_1/\bar{c}_1 = \overline{G}_2/\bar{c}_2$. The relation then takes the form

$$K = p\left(\frac{1}{2}\frac{\overline{G}_1 + \overline{G}_2}{\overline{G}} - 1\right) = p\left(\frac{1}{2}\frac{\bar{c}_1 + \bar{c}_2}{\bar{c}} - 1\right).$$

Whether $\overline{G}_1$ is equal to the temperature of the surface $\overline{G}_1'$ and whether $\overline{G}_2$ is equal to $\overline{G}_2'$ is certainly doubtful. In any case

$\overline{G}_1' > \overline{G}_1 > \overline{G}_2 > \overline{G}_2'$ for such cases as the quantity $\overline{G}_1'$ is assumed greater than $\overline{G}_2'$. As was the case in Sec. 80, one may assume the existence of an *accommodation* coefficient a. Then, as in that section, one has the conditions

$$\overline{G}_1 = \overline{G}_2 + a(\overline{G}_1' - \overline{G}_2)$$

and

$$\overline{G}_2 = \overline{G}_1 + a(\overline{G}_2' - \overline{G}_1).$$

Thus, through addition, $\overline{G}_1 + \overline{G}_2 = \overline{G}_1' + \overline{G}_2'$. As it was assumed that the gas about both plates was in temperature equilibrium with A_2, then $\overline{G} = \overline{G}_2'$. Making use of this and of the relation above, one gets K in the form

$$K = \frac{p}{2}\left(\frac{\overline{G}_1'}{\overline{G}_2'} - 1\right) = \frac{p}{2}\left(\frac{\bar{c}_1'}{\bar{c}_2'} - 1\right).$$

Again,

$$\frac{\overline{G}_1'}{\overline{G}_2'} = \frac{\bar{c}_1'}{\bar{c}_2'} = \sqrt{\frac{T_1}{T_2}},$$

where T_1 and T_2 are the absolute temperatures of the plates A_1 and A_2. Thus $K = \frac{p}{2}\left(\sqrt{\frac{T_1}{T_2}} - 1\right)$, or the pressure $p = \frac{2K}{\left(\sqrt{\frac{T_1}{T_2}} - 1\right)}$ in dynes per cm^2. For small temperature differences this changes to the simple form

$$K = \frac{p}{4}\frac{T_1 - T_2}{T_2} \text{ or } p = 4K\frac{T_2}{T_1 - T_2} \text{ dynes per cm}^2.$$

Thus by knowing T_1 and T_2 and measuring K one obtains the pressure. It is also seen that the momentum transfer per unit time K is proportional to the pressure.

The theory was tested experimentally by using a heated strip of platinum opposite and near one side of a platinum vane suspended at its center by a wire. The force constant of the torsion balance could be determined from its period of oscillation. The suspended vane had a mirror fastened to the suspension by which its deflection could be measured. The temperature of the suspended vane was that of the room. The other strip,

representing A_1, was heated electrically and its temperature determined by its resistance, as it formed one arm of a Wheatstone's-bridge. An example of the results obtained in air for plates 0.55 mm apart is given below. First are given T_1 and T_2. T_2 was measured at the beginning of each experiment before heating T_1, on T_1. From the equation the pressure was calculated from the observed deflections. The pressure, as is seen, is quite constant. The average value 2.28 dynes per cm^2 is to be compared with gage measurements which gave the air pressure as 0.20 dyne per cm^2 and the vapor pressure of the Hg at this temperature as 2.04 dynes per cm^2, the sum giving the observed pressure as 2.24 dynes per cm^2 in good agreement with the absolute manometer.

t_1	31.7	73.3	118.9	155.5	198.5	233.0
t_2	23.4	23.5	23.7	24.1	24.7	25.6
p	2.31	2.39	2.45	2.32	2.27	2.20
t_1	252.0	274.5	299.5	328.9	351.9	376.2
t_2	26.7	28.0	29.6	31.7	34.2	37.2
p	2.19	2.21	2.20	2.23	2.27	2.31

The experiments show that this gage does give good results when the conditions are fulfilled that L, the mean free path, is large compared with the distance between the plates. In the original article more precise forms of the apparatus are described and realms of applicability are discussed. For the scope of this text, however, the material given suffices.

In a later article, von Smoluchowski[20] discusses and revises Knudsen's theory of the absolute manometer. He points out that if this theory using the Maxwell factor f is applied one has Knudsen's expression for the force $K = \frac{p}{2}\left[\sqrt{\frac{T_1}{T_2}} - 1\right]$. If, however, the accommodation coefficient a is used, this equation is only an approximation. Complicated considerations, for which there is no room in this text, taking into account the fact that when a is less than unity it is necessary to deal with four velocities instead of two, lead to a new equation. This takes the form below, which, as is seen, includes the accommodation coefficient:

$$K = \frac{p}{2}\left[\sqrt{\frac{T_1}{T_2}} - 1 + \frac{1 - a}{4(2 - a)^2}\left\{\left(\frac{T_1}{T_2}\right) - 1\right\}^2\right].$$

When a is unity it goes over into the first expression.*

83. Thermal Transpiration.[21]—If two vessels are filled with gas at atmospheric pressures and they are connected by a tube with a diameter large compared to the mean free path, it is usually assumed that if one vessel is warmer than the other the pressures will be the same in both vessels, although the densities vary inversely as the absolute temperatures, that is, in Fig. 50 on one side of the partition A one has a volume V_1, a temperature T_1, a pressure p_1, and a density ρ_1, while on the other side the temperature is T_2, the pressure p_2, the density ρ_2, and the volume V_2. Except for the small region of transition of temperature near A, it is asserted on the basis of observation that $p_1/p_2 = 1$ and that $\rho_1/\rho_2 = T_2/T_1$. This fact appears to be in conflict with the kinetic-theory assumptions. Suppose that the temperature difference T_1 to T_2 could be sharply confined to the plane at A. The kinetic theory would lead one to expect that, since $\bar{c}_1$ is the velocity equivalent to T_1, and $\bar{c}_2$ that equivalent to T_2, the equilibrium would demand $N_1\bar{c}_1 = N_2\bar{c}_2$. This means that $N_1\bar{c}_1/N_2\bar{c}_2 = 1$. Multiplying both sides of the equation by $\bar{c}_1/\bar{c}_2$ one has at once that $N_1\bar{c}_1^2/N_2\bar{c}_2^2 = \bar{c}_1/\bar{c}_2$ and thus that $p_1/p_2 = \sqrt{T_1/T_2}$. But this is in contradiction to the first statement that $p_1/p_2 = 1$. Obviously, both of these statements cannot be true at once. If the kinetic theory is to be correct, it must be shown that the two deductions are not incompatible. The discrepancy is

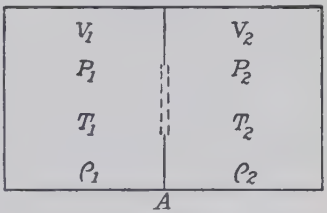

FIG. 50.

* In a later paper Knudsen[62] develops the theory for the torsion on the absolute vane radiometer at very low pressures. This is a torsion balance having two Pt strips with accommodation coefficients a_t' and a_t'' on two sides of each strip in such a fashion as to cause rotation. The pressure difference on the two sides of a strip $p' - p''$ is given by the relation

$$p' - p'' = \frac{1}{4}p\frac{T_1 - T_0}{T_0}(a_t' - a_t'')\frac{1}{1 + \frac{1}{4}(a_t' + a_t'')\frac{T_1 - T_0}{T_0}},$$

T_1 being the absolute temperature of the strip and T_0 that of the large gas space surrounding the strips and vane.

cleared up when it is remembered that, in practice, one does not have an abrupt change in temperature at ordinary pressures. There always exists a transitional layer many mean free paths long in which the equilibrium mechanism may be very complex, and it is probable that the reactions of the walls enter in. Osborne Reynolds[22] was the first to see the consequences of these considerations and to grasp the rôle played by the walls. It was he who gave the name *thermal transpiration* to the phenomenon. If by some manner the temperature transition could be made quite abrupt, then the second law stated, that $N_1\bar{c}_1 = N_2\bar{c}_2$, must prevail and the conditions should be different. Such conditions would exist at low pressures where the temperature differences over a mean free path begin to be significant. Again, as in all such phenomena, the walls play a large rôle, and assist in maintaining large gradients over a mean free path. The proof of the kinetic-theory assumption must lie in phenomena taking place when two bodies of gas are connected by a tube whose dimensions are small compared to the mean free path and in which there is a measurable temperature gradient. In fact, it is observed that under these conditions p_1 is not equal to p_2. A pressure difference is generated which depends on the pressure, molecular weight, coefficient of viscosity, and the diameter of the tube. The phenomenon can be made quite striking if a series of tubes with constrictions be arranged between two volumes and the constriction on the same side be heated to a high temperature. With 10 such tubes heated to 500°C. each, Knudsen achieved a pressure in one bulb 10 times that in the other. At ¼-mm pressure of Hg, and even at 3.5-mm pressure of Hg, he was able to get a pressure difference of 3 mm Hg in the two vessels. If the two vessels be connected by a second unheated tube, this pressure difference will develop a flow of gas from one vessel to the other so long as the heating takes place. The direction of flow is from the region of lower to higher temperature. This must follow at once from the fact that such a flow builds up a pressure p_1 greater than p_2 in the ratio of $\sqrt{T_1/T_2}$ before the equilibrium is established. That the flow must go this way is seen at once also from the fact that N_1 is proportional to ρ_1 and hence to $1/T_1$, while N_2 is proportional to $1/T_2$. If T_1 is greater than T_2, then N_2 is greater than N_1 in the ratio T_1/T_2. The velocities $\bar{c}_1$

and $\bar{c}_2$ are, however, in the ratio $\sqrt{T_1/T_2}$, thus the product $N_1\bar{c}_1$ is less than $N_2\bar{c}_2$ by the ratio $\sqrt{T_2/T_1}$. Hence the flow will take place from cold to hot until the pressure ratio $p_1/p_2 = \sqrt{T_1/T_2}$ builds up to check it. In case this does not occur, the flow will continue indefinitely as long as the gradient exists. If a body could be constructed with capillaries of the order of 10^{-5} cm, then temperature differences existing at atmospheric pressures should succeed in causing a transfer. Such capillaries actually do exist in porous clay vessels. If one of these be provided with a heating arrangement to warm the gas inside and then be sealed off so that its only outlet emerges through water, cold air from outside will pour in and will bubble out through the water. The pressures observed with strong heating may amount to several cm of Hg, and some 100 cm^3 of gas per minute can be made to pass through a bulk of 100-cm^3 volume.

Thus the phenomenon of thermal transpiration is not an insignificant one, and, further, it results in completely removing the apparent paradox facing the kinetic theory by an analysis of what occurs in the region of the gradient. It is therefore worth while to study it briefly before closing the subject of low-pressure phenomena. To begin the analysis, the phenomenon may be regarded as follows: If a plate were placed in the tube, a pressure difference due to the difference between $N_1\bar{c}_1$ and $N_2\bar{c}_2$ would be set up. If the plate were free to move, it would encounter a force against the walls of the tube. From the kinetic theory it is seen that, even were the plate absent, the walls would receive a tangential force when the temperature gradient exists. To study this assume a tube with a mild temperature gradient down it such that the density does not change appreciably over points a few free paths apart. Then the molecules striking it from one direction (*i.e.*, the warmer side) give it an impulse proportional to $n\bar{c}_1$ and those from the other direction give it an impulse proportional to $n\bar{c}_2$. If the temperature gradient is small, the number of impacts dn which unit surface receives from the solid angle $d\omega$ at an angle α is $dn = \frac{d\omega}{4\pi} N\bar{c} \cos \alpha$. Let it be assumed that $d\bar{c}/dl$ decreases in the direction of the tube, where dl is an element of length of the tube of the order of magnitude of the free path λ. Here also $\bar{c}$ is the average velocity of the molecules in the cross section at the element, assuming $\bar{c}$ constant over the area of the cross

section. Assume a rectangular coordinate system with origin at the surface. The l-axis is along the tube, and the z-axis is normal to the surface. The axis λ of the solid angle makes an angle α with z and an angle β with l, where λ is the mean free path. The average velocity of the molecules will be the velocity corresponding to λ, and this velocity is $\bar{c} + \frac{d\bar{c}}{dl}\lambda \cos \beta$ when α is to the right of the yz plane and $\bar{c} - \frac{d\bar{c}}{dl}\lambda \cos \beta$ when it is to the left of this plane, if $d\bar{c}/dl$ is assumed negative. In this case λ is small compared to the diameter of the tube. The momentum received per cm^2 of surface for impacts to the right of the cross section in the yz plane for the solid angle $d\omega$ is

$$mdn\left(\bar{c} + \frac{d\bar{c}}{dl}\lambda \cos \beta\right) \cos \beta.$$

From the opposite side of the plane the momentum received from a similar solid angle is

$$mdn\left(\bar{c} - \frac{d\bar{c}}{dl}\lambda \cos \beta\right) \cos \beta.$$

The net momentum received per second per cm^2 from the gas as a whole for $d\omega$ is, therefore,

$$dM' = 2m\, dn \frac{d\bar{c}}{dl}\lambda \cos^2 \beta,$$

whence

$$M' = 2m \int \frac{d\bar{c}}{dl}\lambda \cos^2 \beta dn,$$

if it be assumed that the molecules leaving the surface are reflected equally in all directions. Putting the value of dn into M' and integrating for M', the expression is obtained:

$$M' = -\frac{1}{16} N m \bar{c} \lambda \frac{d\bar{c}}{dl}.$$

Introducing Maxwell's distribution of velocity then*

* This step is not obvious. Knudsen uses $\bar{c}$. The product $\bar{c}d\bar{c}$, he however assumes, requires that the root-mean-square velocity C be implied. To continue the use of the average velocity $\bar{c}$, the expression must be multiplied by $\frac{3\pi}{8}$ as $\sqrt{\frac{3\pi}{8}}\bar{c} = C$.

$$M = -\frac{3\pi}{128} N m \bar{c} \lambda \frac{d\bar{c}}{dl}.$$

As $Nm\bar{c}\lambda = \eta/0.30967$ (see Sec. 59), where η* is the coefficient of viscosity, this becomes

$$M = \frac{-3\pi\eta}{128(0.30967)} \frac{d\bar{c}}{dl}.$$

This is the tangential force exerted by the gas on unit surface of the tube. If this force just balances the force of the molecules, equilibrium results and there is no streaming motion. Thus if there is no streaming in the tube

$$2\pi RM - \pi R^2 \frac{dp}{dl} = 0,$$

where R is the radius of the tube. Whence the pressure gradient existing can be found at once as

$$\frac{dp}{dl} = \frac{3\pi\eta}{64(0.30967)R} \frac{d\bar{c}}{dl}.$$

Now

$$\bar{c} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{T}{273\rho_0}},$$

where T is the absolute temperature and ρ_0 is the specific gravity of the gas at 0° for a pressure of 1 dyne per cm². As η varies with the temperature, according to Sutherland's formula one has

$$\eta = \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}} \sqrt{\frac{T}{273}} \eta_0 \text{ (see Sec. 63).}$$

In H_2 gas, $C = 83$, $\eta_0 = 841 \times 10^{-7}$, and $\rho_0 = 88.62 \times 10^{-12}$. Also

$$\frac{1 + \frac{C}{273}}{1 + \frac{C}{T}}$$

can be set at 1.12 for two temperatures $T_1 = 800°$ and $T_2 = 300°$, whence solving, one has $R\frac{dp}{dT} = 0.0139$. For $R = 0.0187$,

* It is not clear which value for η is used. In later work Knudsen uses Chapman's value, $\eta = 0.49 Nm\bar{c}\lambda$. Hence too much emphasis must not be placed on numerical agreement.

for the temperature difference 500°, $p_1 - p_2 = 371.9$ dynes per cm². With 10 such tubes in series separated by large-diameter tubes, $p_1 - p_2 = 3{,}581$ dynes per cm². The observed pressure difference in an actual experiment gave $p_1 - p_2 = 3{,}693$ dynes per cm².

As M is independent of pressure, this calculated pressure difference should be independent of the absolute values of p_1 and p_2. Experimentally, the observed pressure difference rapidly diminishes with increasing p.

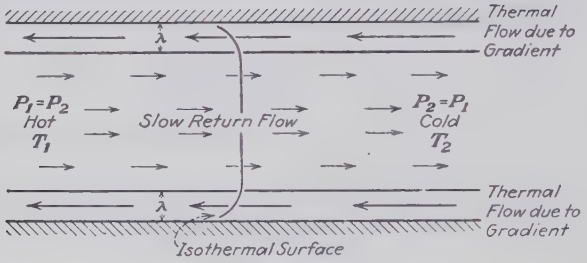

FIG. 51.

To explain this case, the hypothesis of equal numbers of impacts from both sides, used in arriving at an expression for M, must be given up. This change would be expressed by assuming that at higher pressures streaming actually occurs in the tube and that this streaming is of such a nature that the wall receives less momentum than through M, for it is obvious that, if N_1 and N_2 were different, streaming would occur. Since this streaming goes from cold to hot, momentum due to the streaming gas would also reach the walls and this would be, in a sense, opposite to the momentum received due to $\bar{c}_1$ being greater than $\bar{c}_2$ going from hot to cold. Also this streaming motion must progress in the direction of increasing temperatures, for it is in this direction that the walls act on the nearest gas layers with their tangential forces. As in equilibrium the gas mass as a whole must be at rest, there must therefore be a streaming on the inside of the tube in a sense opposite to the streaming along the tube walls, when this streaming along the tube walls occurs, for the streaming along the wall would build up a pressure difference, the pressure building up on the hotter side. The return of this moved gas mass which results from the walls, in view of the pressure difference built up, will naturally take place in the interior sections of the tube where the only resistance to overcome is the viscous action of the gas

(see Fig. 51). It is seen that if such an action takes place the pressures in the two vessels will be equal, while, owing to the difference between $N_1\bar{c}_1$ and $N_2\bar{c}_2$, a streaming does take place. This, of course, will occur only at higher pressures. At the lower pressures, where the free paths begin to compare with the tube size, the simple equations deduced above hold, and a pressure difference will be maintained.

The flow under these conditions may now be investigated quantitatively. It is first necessary to calculate M, the momentum transfer, which every cm² of the wall receives per second through the temperature drop, because the molecules coming from one side have a higher velocity than those from the other side. In the present case, $\bar{c}$ is not the same for all molecules coming from any point in the cross section of the tube. The isothermal surfaces will now make an angle with the walls. The velocity of the gas layers must decrease in the direction of the temperature gradient from the axis to the walls. Hence the isothermal surfaces will make an acute angle with the walls in the direction of the temperature gradient. This will make the number of molecules which come from the left with particularly high velocities greater than those which come from the right with particularly low velocities. Thus the *old* expression for M is numerically less than the real momentum M received by the unit surface, regardless of the momentum which comes from the streaming gas along the surface. The new M may therefore be set as

$$M = -\frac{3\pi}{128} N m \bar{c} \lambda \frac{d\bar{c}}{dl} k_1 = -\frac{3\pi}{128} p \rho_1 \bar{c} \lambda \frac{d\bar{c}}{dl} k_1.$$

If R/λ is small, $k_1 = 1$, and if it is large, k_1 converges to a value between 2 and 3. Again $Nm = \rho$ was set as equal to $p\rho_1$, where ρ_1 is the density of gas at 1 bar (dyne per cm²) and p is the pressure in bars. Finally the equation in terms of $\bar{c}$ enables one to write $\bar{c} = \sqrt{8/(\pi\rho_1)}$, while $d\bar{c}/\bar{c} = dT/2T$, whence

$$M = -\frac{3}{32} p \lambda \frac{1}{T} \frac{dT}{dl} k_1.$$

One must next correct for the momentum given the tube by the gas stream flowing from cold to hot, *i.e.*, in a positive sense. This flow is not zero at the walls, and it therefore represents a flow with a slip term. In the center of the tube there is a very

slow return flow whose velocity compared to the flow at the walls is 0. One may call the velocity at the walls relative to the axis V and identify it with a slip term in the expression for the flow of gas down a tube. In the study of the flow of gases down a tube at pressures in the region where the transpiration is of interest, Knudsen showed that

$$T = \frac{Q_t}{p_1 - p_2} = \frac{G}{\rho_1(p_1 - p_2)} = ap + b\frac{1 + c_1 p}{1 + c_2 p},$$

where G is the mass flow per unit time (see page 296). The constants a, b, c_1, and c_2, Knudsen identified with elements involved in the flow. The coefficient a is identified with the normal Poisseuille flow* and corresponds to the return flow, its value being $a = \frac{\pi}{8}\frac{1}{\eta}R^4$ when referred to mass flow in a tube of radius R with a coefficient of viscosity η. The term b represents the slip term which goes over into the Knudsen flow at very low pressures and a simple slip term at higher pressures. The whole slip term was found to be closely approximated by the expression $b\left(\frac{1 + 0.81\frac{5R}{\lambda}}{1 + \frac{5R}{\lambda}}\right)$ which is of semi-empirical origin. As the deviations from the simple theory for transpiration were observed at higher pressures where $2R/\lambda$ was rather large, a first approximation of this expression for b can be used for $5R/\lambda >> 1$. In this case the slip term reduces to 0.81 b. Thus the mass flow down the tube at a slip velocity V, defined by the mass flow $\pi R^2 \rho V$, must equal the slip velocity term in G which is 0.81 $b\rho_1\frac{dp}{dl}$. Hence $\pi R^2\rho V = 0.81\ b\rho_1\frac{dp}{dl}$. On the other hand, equilibrium demands that the Poisseuille flow down the center just compensate the slip flow at the walls. Thus $ap\rho_1\frac{dp}{dl}$, the Poisseuille mass-flow term, must equal the slip flow 0.81 $b\rho_1\frac{dp}{dl}$. Hence $V = \frac{ap\rho_1}{\pi R^2\rho}\frac{dp}{dl}$, with $a = \frac{\pi}{8}\frac{R^4}{\eta}$, which gives

* This use of a is slightly different from the use of a on page 297, where a was set as, $a = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}$. The a here used omits $\frac{1}{L}$, as this appears in the expression dp/dl.

$V = \frac{1}{8}\frac{R^2}{\eta}\frac{dp}{dl}$. There is, however, another factor which must be taken into account. In the study of the slip it was found that, owing to the action of a velocity gradient increasing from the walls to the axis, the slip velocity is not just the value V inferred from v_0 as deduced by Maxwell (page 287), but somewhat greater than this value as the more axial molecules transfer momentum from the faster moving layers to the wall layer. In the régime of low pressures Knudsen identifies the correction for this with the factor $\frac{1 + \frac{5R}{\lambda}}{1 + 0.81\frac{5R}{\lambda}}$, which in the pressure region of interest at present (p such that $5R/\lambda >> 1$) becomes $1/0.81$. Thus the V used in flow with slip in this pressure region must be corrected by dividing it by 0.81. In the case of thermal transpiration, however, the conditions are the reverse of normal flow and the velocity at the wall is greatest, while at the center it is reversed in sense and to all intents and purposes is practically 0. Hence assuming conditions essentially similar in the case of transpiration as in normal flow except for the fact that V is *reduced* by the inner flow, Knudsen feels justified in writing the slip term into the expression for momentum transfer due to flow along the wall as 0.81, the value calculated before. Hence the actual slip velocity at the wall, $v = 0.81V = \frac{0.81}{8}\frac{R^2}{\eta}\frac{dp}{dl}$. It was shown on page 291 that B, the momentum transfer to the walls from a mass of gas moving with an average velocity v down the walls, was given by

$$B = \frac{3\pi}{32}Nm\bar{c}v.$$

As seen above, v can be replaced by the velocity of slip V, provided a correction be made for the retardation by the more axial portions of the flow. Hence

$$B = \frac{3\pi}{32}Nm\bar{c}\frac{0.81}{8}\frac{R^2}{\eta}\frac{dp}{dl} = 0.81\frac{3}{32}\frac{\sqrt{\pi}}{8}\frac{\sqrt{\rho_1}}{\eta}R^2p\frac{dp}{dl}.$$

In terms of the Jeans coefficient of viscosity (page 214), Knudsen[81] in a more recent paper transforms this expression as follows:

$$\eta = 0.49Nm\bar{c}\lambda$$

whence

$$\lambda = \frac{1}{0.49}\sqrt{\frac{\pi}{8}}\frac{\eta}{p\sqrt{\rho_1}},$$

and hence

$$B = \frac{3\pi}{256}\frac{0.81}{0.49}\frac{R^2}{\lambda}\frac{dp}{dl}.$$

Thus each unit length of tube receives momentum in the amount $2\pi R(M + B)$ per second, so that flow equilibrium is expressed by

$$2\pi R(M + B) + \pi R^2\frac{dp}{dl} = 0,$$

whence

$$2\pi R\left\{-\frac{3}{32}p\lambda\frac{1}{T}\frac{dT}{dl}k_1 + \frac{3\pi}{256}\frac{0.81}{0.49}\frac{R^2}{\lambda}\frac{dp}{dl}\right\} + \pi R^2\frac{dp}{dl} = 0$$

and

$$\frac{dp}{dT} = \frac{1}{\frac{8}{3}\frac{1}{k_1}\frac{R}{\lambda} + \frac{\pi}{16}\left(\frac{0.81}{0.49}\right)\frac{R^2}{\lambda^2}\frac{1}{k_1}}\frac{p}{2T}.$$

Knudsen has shown this to be about correct for large values of R/λ. Hence the expressions for thermal transpiration at low and high pressures, R/λ very large and very small, have been determined. In the later paper Knudsen[81] attempts to improve the expression for thermal transpiration in the intermediate range. In the first edition of this book it was shown that for pressures where $R/\lambda \sim 1$, one must take into account the collisions of molecules which have had their last collision with the walls, while others have collided with molecules in the gas space. In this case an approximate expression was obtained which read

$$\frac{dp}{p} = \frac{1}{1 + \frac{2R}{\lambda}}\frac{d\bar{c}}{\bar{c}},$$

so that

$$\frac{dp}{dT} = \frac{1}{1 + \frac{2R}{\lambda}}\frac{p}{2T}.$$

This expression, as Knudsen shows in his later article, may be related to the high-pressure equation by an empirical expression

$$\frac{dp}{dT} = \frac{1}{\left(1 + \frac{a'R}{\lambda}\right)^2} \frac{p}{2T}.$$

From the conditions at higher pressure Knudsen determined the best empirical expression for the term a', which varies with R/λ. This expression is $a' = a\frac{1 + b\frac{R}{\lambda}}{1 + c\frac{R}{\lambda}}$, in which a, b, and c are constants with $c > b$.

It must next be noted that λ is a function of p and T. Calling $\lambda = p\lambda_1$ where λ_1 is the mean free path at a temperature T and a pressure of 1 dyne per cm^2, and assuming the coefficient of viscosity for H_2, with which he worked, to be given by $\eta = \eta_0(T/273)^{0.682}$ by setting $\lambda p = \frac{1}{0.49\sqrt{8}} \frac{\eta}{\sqrt{\rho_1}} = \frac{1}{0.49\sqrt{8}} \frac{\eta_0}{\sqrt{\rho_0}} \left(\frac{T}{273}\right)^{1/2}$ he obtained $\frac{1}{\lambda} = \frac{p}{\frac{1}{0.49\sqrt{8}} \frac{\eta_0}{\sqrt{\rho_0}} \left(\frac{T}{273}\right)^{1.182}}$, where ρ_0 is the density of H_2 at 1 bar (dyne per cm^2) and 273°C. Comparing the observed values of $\frac{\Delta p}{\Delta T}\left(\frac{2T}{p}\right)$ representing the expression to be tested with those obtained from approximate values of the constants, he was able to evaluate a, b, and c for H_2 with some success. The values found were $a = 2.46$, $b = 3.15$, $c = 24.6$. Thus he found that the equation for thermal transpiration for H_2 in cylindrical tubes of radius R was given quite adequately by the semi-empirical expression

$$\frac{dp}{dT} = \frac{1}{\left(1 + 2.46\frac{R}{\lambda}\frac{1 + 3.15\frac{R}{\lambda}}{1 + 24.6\frac{R}{\lambda}}\right)^2} \frac{p}{2T},$$

with $1/\lambda = 0.08753p(273/T)^{1.182}$ in the intermediate pressure range.

For the case where dp/dT was so great that the differential form could not be used, Knudsen integrated the equation in a simple fashion. It appeared from this expression that the differ-

ential form is quite accurate in the region between $293 \pm 20°$. The general equation gives satisfactory values within 1 per cent, and it appears to hold at low temperatures within the accuracy which can be attributed to the certainty in the values of η. Finally, it is to be noted that this accurate semi-empirical equation was developed on the basis of the theoretical expression

$$\frac{dp}{dT} = \frac{1}{1 + 2\frac{R}{\lambda}} \frac{p}{2T}.$$

For small values of R/λ, but such values as are not vanishingly small, it was assumed that the above equation held. The empirical equation reduces in this case to

$$\frac{dp}{dT} = \frac{1}{1 + 2a\frac{R}{\lambda}} \frac{p}{2T}$$

which can agree with the theoretical equation only if $a = 1$. Experiments show, however, that $a = 2.46$ in this region. The explanation of this discrepancy is not at hand. It may represent a defect in the theory or it can represent an error in the evaluation of a caused by adsorption phenomena. He concludes that if one can be free from difficulties due to adsorption (caused by gas liberation at heated points and adsorption at cool points), and if the theory is accurate, the method gives a new type of evaluation of the mean free path, λ, in which λ is compared directly to the tube radius. One can thus assume that the problem of thermal transpiration has been analyzed and developed to a satisfactory degree of precision, even though as in all this intermediate pressure region the mathematical difficulties force a quasi-empirical form on the equations obtained.

84. Radiometric Forces in Gases.—It was remarked in Sec. 82, where the force between two plates at different temperatures in gases at very low pressures was derived, that this phenomenon might be classed with the various other radiometric phenomena. In the sense that the forces involved are due to molecular impacts depending on differences of temperature at reduced gas pressures, they might be identified as belonging to the same class of phenomena as those usually termed radiometric. From the mechanical point of view, however, the resulting mechanisms are radically different in the two cases. The radiometric effects

which have mostly been used for measurements of radiation intensity are most effective and prominent in a pressure régime much higher than the régime investigated by Knudsen. Their maximum efficiency lies at about 0.05 mm of Hg, the exact location of the maximum depending, of course, fundamentally on the dimensions of the apparatus. Aside from the fact that the theoretical treatment depends largely on questions of design and has been but incompletely worked out, the pressure régime involved makes it scarcely more than deserving brief mention in this chapter.

The repulsion of a radiated body under radiation was first observed by Fresnel. W. Crookes studied it beginning in 1873, and devised many different forms of the device. Among these was the well-known vane radiometer, in which light vanes blackened on one side were mounted about an axis free to rotate in a partially evacuated space. These radiometers are frequently seen in opticians' windows and are called after their discoverer the Crookes radiometer. Crookes found that the radiometric force was a function of the gas pressure, depended on the absorption coefficient of the wing surface, and was proportional to the intensity of radiation. Schuster showed that this was not due to light pressure. He suspended the chamber as well as the vane and found that the vane was moved relative to the chamber. This indicates that it was a relative force between vane and walls, and not the light pressure, which acted. Had it been light pressure, both vane and chamber would have been displaced. Donle investigated the forces keeping the pressure constant. The information gained by him and others, notably Nichols and Rubens,[34] and Nichols and Hull, dealt chiefly with the radiation side of the phenomenon and Nichols[35] developed a very useful radiometer for the study of radiant energy based on this action.

Even as early as 1874 the effect was ascribed as being due to the unequal bombardment of molecules produced on the two sides by differences of temperature. That actions of this sort do occur was seen in Sec. 82, where Knudsen's absolute manometer was discussed. The pressures where such simple actions occur are, however, much lower than those obtaining in Crookes' experiments, and it was soon noticed that the explanation given was in contradiction to the kinetic theory at the higher pressures. Many attempts were made in those days to explain and derive

quantitative theories for the phenomenon which would fit experimental facts. These largely failed for two reasons: In the first place, the pressure measurements until 1909 were not reliable, for it is only since Knudsen's work that low-pressure measurement has reached any degree of precision. In the second place, very few of the experiments were ever correlated with the temperature measurements on the vanes. The importance of the latter will be seen in later discussion. As a result of the analyses of the phenomenon, two rival schools were set up. The first group contended that repulsion was due to a surface-area effect, and was proportional to the blackened surface. This was contended by G. J. Stoney[23] and by Fitzgerald.[24] On the other hand, Maxwell,[19,33] with his remarkably clear vision, contended that the large portions of the areas of the vanes were inactive and that it was only at the edges that one had any stress arising from inequality of temperature in the gas. O. E. Meyer concurred with Maxwell in this view. On Maxwell's theory, therefore, no forces other than edge effects could cause the pressure. Miss Edith Einstein again attempted to derive a theory for forces proportional to the whole surface, in which she carried on Maxwell's calculations, using higher order terms. Of this, more will be said later.

Subsequently interest again revived in this field, largely through the experimental work of Gerlach and Westphal,[25] Westphal[26] and Gerlach[27] independently, and finally Westphal.[28] Westphal in 1919 deduced a theory of the effects which virtually stood until 1924. In 1924, two theoretical papers appeared. One was due to Hettner and Czerny[29] and contained an experimental test of some of their conclusions. It dealt with the repulsion type of radiometers, such as used by Nichols in radiation measurements. The other paper was by A. Einstein[30] and dealt in a semi-quantitative fashion with the Crookes type of radiometer. The content of these papers gives today a clear picture of the nature of the usual radiometric phenomena, and they will form the basis of this section. Suffice it to state that both indicate the predominance of the edge of the vanes in the two phenomena, thus establishing the correctness of the view set forth by Maxwell[19,33] in his paper. The work of Einstein has received partial experimental confirmation by Marsh.[31]

Just preceding the work of Hettner and Czerny, Miss Edith Einstein[32] worked out a theory of the radiometer for pressures

where the free path was not greater than the dimensions of the plates. This theory gave the variations of radiometric forces with pressure which were observed experimentally. The theory, however, led to radiometric forces proportional to the square of the heat flow in the gas. This would mean that the magnitude of the forces should be proportional to the square of the intensity of illumination, while the observed forces are proportional to the first power of the intensity. Furthermore, Czerny made measurements of the absolute magnitude of the radiometer forces which showed them to be 10^4 times greater than those calculated from Miss Einstein's theory. From this Hettner and Czerny concluded that, while the effect predicted by Miss Einstein probably existed, it constituted but a small fraction of the observed effect.

In seeking for an explanation, Hettner and Czerny reverted back to the theory of Maxwell discussed in Sec. 77, in which Maxwell concluded that, because of temperature gradients at the surfaces of solid bodies, tangential forces could be set up which would produce a streaming along the surface. Such surface gas currents Maxwell suspected might be the cause of the radiometric effects, and were the basis of his suspecting the edges as being the seat of action. The tangential forces assumed by Maxwell were, however, proportional to the second derivative of the temperature. They would, therefore, although playing a rôle, cause small effects compared to forces produced by the first derivative of the temperature. Maxwell[33] had also calculated forces depending on the first derivative, but had not applied them to the radiometer.

The forces last referred to are, however, nothing other than the familiar forces discussed in the preceding section, and which led to the phenomenon of thermal transpiration. For very low pressures, this phenomenon was worked out by Knudsen, who also discussed the case at higher pressures. His considerations were worked out, however, for special cases, and were not particularly adapted to the problem in hand. Furthermore, they were more or less first-order approximations. Maxwell's considerations were much more general. In his time, the relations between molecular impacts and surfaces were not known. The later knowledge enabled Hettner and Czerny to carry the latter calculations through in a more rigorous fashion than had been done before. They, in general, used Maxwell's method, which is based on the development of the distribution of velocity

functions as powers and products of the velocity components. As this method in the form used is beyond the scope of this text, the results of their calculations only will be given. Calculation shows that the velocity of the layer next the surface relative and parallel to it, u_2, is given by the equation

$$u_2 - \zeta \frac{du_2}{dz} = \frac{3}{4} \frac{\eta}{\rho T} \frac{\partial T}{\partial x}.$$

In this equation ζ is the coefficient of slip of the gas, $\zeta = \sqrt{\frac{\pi}{2}} \sqrt{\frac{M}{RT}} \frac{\eta}{\rho}$ (Sec. 77), ρ is the density, η the coefficient of viscosity, T the absolute temperature, and z is a length along the axis normal to the surface, while x is the length along the axis chosen parallel to the temperature gradient. If for η one put K, the coefficient of heat conductivity for a monatomic gas, where $\frac{K}{\eta} = \frac{15}{4} \frac{R}{M}$, the equation becomes

$$u_2 - \zeta \frac{du_2}{dz} = \frac{1}{5} \frac{K}{p} \frac{\partial T}{\partial x}.$$

This equation gives the u_2 the same sign as the $\partial T/\partial x$, which signifies that the velocity is directed in the same sense as $\partial T/\partial x$ is positive. That is to say, u_2 goes from cold to hotter points along the surface. If one neglect the slip term, $u_2 = \frac{3}{4} \frac{\eta}{\rho T} \frac{\partial T}{\partial x}$. This for $\partial T/\partial x = 1°$ for air at room temperature has the value $392/p$ cm/sec. If the pressure p is 392 dynes per cm^2, (0.294 mm of Hg), the velocity will be 1 cm per sec. It is, therefore, obvious that currents with considerable velocities can be set up for even small temperature gradients.

To compare their result with Knudsen's it is essential to calculate the tangential force $-p_{12}$ exerted on the wall by the gas. Calculation gives

$$-p_{12} = \frac{\eta}{2} \frac{\partial u_2}{\partial z} - \frac{3}{4} \frac{\eta}{\sqrt{2\pi}} \sqrt{\frac{R}{MT}} \frac{\partial T}{\partial x} + \frac{\eta}{2\zeta} u_2.$$

From the expression for u_2 above, $\partial u_2/\partial z$ can be eliminated and then

$$-p_{12} = -\frac{3}{2} \frac{\eta}{\sqrt{2\pi}} \sqrt{\frac{R}{MT}} \frac{\partial T}{\partial x} - \frac{\eta}{\zeta} u_2 = \eta \frac{\partial u_2}{\partial z}$$

Knudsen calculated $-p_{12}$ in Sec. 83 as

$$-p_{12} = -\frac{3\pi\eta}{128 \cdot 0.31}\frac{\partial c}{\partial x} \text{ for a resting gas.}$$

This transforms into

$$-p_{12} = -0.19\eta\sqrt{\frac{R}{MT}}\frac{\partial T}{\partial x}$$

while Hettner and Czerny's equation yields

$$-p_{12} = 0.30\eta\sqrt{\frac{R}{MT}}\frac{\partial T}{\partial x}.$$

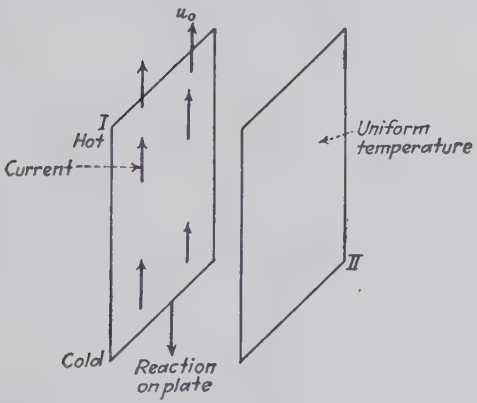

FIG. 52.

The difference lies only in the numerical factors 0.30 and 0.19. Knudsen's experiments gave twice the theoretical value for $-p_{12}$, and thus Hettner and Czerny's value is distinctly more satisfactory.

To carry this over to the case of a radiometer, consider the system shown in Fig. 52. Plate I is heated with a temperature gradient such that the upper edge is warm while the lower edge is cold. Opposite it a cm away is plate II of uniform temperature throughout. There will be at the surface I a current from cold to hot of velocity u_0. The reaction to this will be a force on the vane downward. Call u_a the value of u_2 at the plate II, that is a cm distant from u_2. The velocity u_2 will then be given at any point z by

$$u_2 = u_0 + (u_a - u_0)\frac{z}{a}.$$

The hydrodynamic equations between the plates are fulfilled, together with the velocity conditions imposed by the equations deduced, when

$$u_0 - \zeta\frac{u_a - u_0}{a} = \frac{3}{4}\frac{\eta}{\rho T}\frac{\partial T}{\partial x},$$

and $u_a + \zeta\dfrac{u_a - u_0}{a} = 0$, whence it follows that

$$(u_a - u_0)\left(1 + \frac{2\zeta}{a}\right) = -\frac{3}{4}\frac{\eta}{\rho T}\frac{\partial T}{\partial x}.$$

Under the conditions where the equation applies, a must be large compared to a free path, while the coefficient of slip has the dimensions of a free path. Thus $2\zeta/a$ is negligible. The tangential force of reaction on the plane is then per cm^2

$$-p_{12} = \eta\frac{\partial u_2}{\partial z_1} = \frac{\eta}{a}(u_a - u_0) = -\frac{3}{4}\frac{\eta^2}{a\rho T}\frac{\partial T}{\partial x}.$$

As one can measure p_{12}, and as a, ρ, T, η, and $\partial T/\partial x$ are known, the theory may be tested.*

It is now the question whether these tangential forces may not be able to explain quite a number of other of the radiometric effects. A qualitative discussion of a few of the more common types will be taken up at this point:

1. Rubens and Nichols designed a radiometer of the type shown diagrammatically in Fig. 53. Plate I is blackened and illuminated. Plate II is a conducting plate, or one that is uniform in temperature and not heated. It happens from the geometry of the system that the illuminated plate has a temperature gradient from the center C to the edges. The existence of such gradients has been proved experimentally by Marsh[31] on blackened radiometer vanes of mica, by direct measurement. He observed, at 1.2-, 0.4-, and 0.04-mm pressure, temperature differences of 0.16, 0.24, and 0.28° on two points, 1 cm apart, of a vane of mica 0.45 mm thick when illuminated on the blackened side by light from a Point-O-Light lamp. The one point chosen was 1 mm from the edge, the other at the center of the vane. As a result of this gradient the gas will flow along the heated vane from the cooler edges to the center. As the opposite vane is

* This radiometric force has been measured experimentally by Hettner and Czerny[90] for He, H_2, and air and has been found to agree in magnitude and variation with that deduced.

cold and uniform in temperature, the return current of gas will flow from the center outward along the surface of plate II. Such a flow of gas as indicated by the arrows will, owing to gaseous viscosity, build up a pressure in the center. Thus one will have repulsion between the two plates. Hettner and Czerny calculated the radiometric force for this case, but do not give it. It is stated that the forces in this case for the same ratio of plate

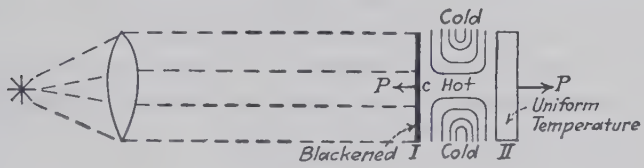

FIG. 53.

area to plate distance are greater than the one previously calculated for the lateral thrust on the vane.

2. If both surfaces I and II are illuminated, the currents then flow along both surfaces from the edges to the center. The return currents occur in the center. This arrangement therefore simply gives greater forces of repulsion compared to the hot and cold plates.

Perhaps one of the most striking proofs of this mechanism is in those forms of radiometers where the motion can take place in the direction of the sharp edges. As the edge is cooler than the central part, it will cause the metal to be given an impulse in the direction of the edge while the gas streams in the opposite sense. An amusing form of such a radiometer is one made of two half cylinders of bright tin, mounted on arms placed on a pivot. On illumination, these rotate about the pivot with the concave sides leading.

The actual calculation of the forces and their quantitative verification, however, must be confined to simple cases. It is quite clear that the conditions which determine this type of radiometric action are entirely too complex to permit of any exact calculation. Hettner[58] and, independently but later, Sexl[84] have calculated the radiometric forces on certain solids of simple geometric form suspended in a large gas space. Hettner works out the equations, using hydrodynamical considerations for the case of a sphere. Sexl works out the case of an ellipsoid of rotation which can be reduced to the case of a sphere and of a plane circular disc. Both of these calculations are exact and

rigorous and the equations agree in the case of the sphere, except for the numerical coefficient which is slightly different, due to a different definition of the mean free path in the two cases. The theories are tested in their application to the case of the photophoresis discovered by Ehrenhaft[89] and lately quantitatively investigated by Mattauch.[88] In this case, particularly at lower pressures, approximations must be made for the fact that at very low pressures the force is a surface effect and varies with p, while at higher pressures it is an edge effect and varies as $1/p$. Knudsen,[62] in a later paper, makes a similar approximation for the case of intermediate pressures, all three approximate solutions leading to the experimentally discovered law of Westphal[36] in this region, which says that $\frac{1}{K} = \frac{p}{a} + \frac{1}{bp}$, where K is the force and a and b are constants. If in this equation one set $\sqrt{a/b} = p_0$, and $\log p/p_0 = x$, then $K = \frac{\sqrt{ab}}{e^x + e^{-x}}$, which is the symmetrical law of Westphal giving a maximum at $x = 0$ or $p = p_0$.

The analysis of Sexl[84] proceeds as follows. He considered an ellipsoid of revolution whose axis of symmetry lay along the x-axis, which also represents the axis of propagation of the radiant energy. The surface of the ellipse thus receives a temperature gradient giving rise to the Osborne Reynolds surface streaming. The forces produced by such flow can, for the case of the ellipse, be studied from the standpoint of classical hydrodynamics. The problem thus resolves itself into three steps: (1) the establishment of the velocity distribution law for a gas in which there exists a temperature and velocity gradient; (2) the calculation of the kinetic-theory boundary conditions at the surface of the ellipsoid; (3) the solution of the hydrodynamic problem. The calculation of item (1) follows in essence the Boltzmann H-function method of approach which Epstein has shown to be particularly adapted to this type of problem, and which is independent of the nature of the intermolecular impacts. This generalized calculation is beyond the scope of this text and must therefore be omitted. As regards the interaction of the molecules with the wall and the surface, Sexl assumes that the fraction f of the molecules striking them is diffusely reflected in temperature equilibrium with the wall and according to the well-known cosine law, while the fraction $1 - f$ molecules is elastically

reflected with the original energy distribution, the normal component of velocity being reversed. This is essentially one of the approaches to the accommodation problem taken by von Smoluchowski (see page 323) and the one which was shown to be the least satisfactory. It transfers the concept of Maxwell's f for momentum exchange with a surface to the one for energy exchange. It is doubtful whether the use of f exclusively is correct. Actually for most solid vanes $f = 1$, while a, the accommodation coefficient, is different from unity, particularly if one has different surfaces on the two sides of the vane. Thus for momentum transfer the use of an f is justified, but it is not justified for the evaluation of the energy of the escaping or reflected molecules. Application of the law of conservation of momentum to the case yields a value for the velocity of the gas at the surface of the ellipsoid, assuming a plane surface. The expression for the streaming velocity is of the same form as that obtained by Hettner.[58] The constant of Sexl's equation is, however, different as might be expected.

Application of the hydrodynamical principles under these conditions gives the radiometric force R on the ellipsoid of minor axis b and major axis a as

$$R = \frac{14.72}{n+5}\frac{pL^2}{T}\delta T b^2 \frac{2-\alpha_0}{\chi_0 + \alpha_0 a^2}.$$

If the ellipsoid degenerates into a sphere, $a = b$, $\alpha_0 = \frac{2}{3}$, $\chi_0 = 2a^2$. This gives $b^2\dfrac{2-\alpha_0}{\chi_0 + \alpha_0 a^2} = \dfrac{1}{2}$. Whence the force on a spherical radiometer is

$$R_{sph.} = \frac{7.36}{n+5}\frac{pL^2}{T}\delta T.$$

Here L is the mean free path, p the pressure, T the absolute temperature, and n represents the number of degrees of freedom of rotation and vibration active, *i.e.*, $n = 0$ for a monatomic gas (see Sec. 91). This expression agrees with that derived by Hettner[58] which reads

$$K = \frac{3\pi}{2}\frac{\eta^2}{\rho T}\delta T = 4(0.49)^2\frac{pL^2}{T}\delta T.$$

Hence, except for a numerical coefficient coming from the fact that the definitions of the mean free paths used in the two cases were different, the two equations agree.

The interpolation of this equation between this high-pressure form and the Knudsen low-pressure form predicts the results of Mattauch[88] on the photophoresis of small spheres quite well. If a be made so small that the ellipsoid degenerates into a disc of radius b, $\alpha_0 = 2 - \pi\frac{a}{b}$, $\chi_0 = \pi ab$, such that $b^2\frac{2 - \alpha_0}{\chi_0 + \alpha_0 a^2} = 1$ and R_{disc} is given by

$$R_{disc} = \frac{14.72}{n + 5}\frac{pL^2}{T}\delta T.$$

If I is the radiant energy falling on the surface per second, if K_i is the heat conductivity of the plate and δ its thickness, $K_i\frac{\delta T}{\delta} = I$, whence $\delta T = \frac{\delta}{K_i}I$ and one has

$$R_{disc} = \frac{14.72}{n + 5}\frac{\delta}{K_i}I\frac{pL^2}{T}.$$

This agrees very closely with an equation of Epstein[86] for a disc which is conducting.

According to Sexl this equation agrees with experiment in that it makes R proportional to $1/p$ (L is proportional to $1/p$), to I, and to the nature of the gas through L^2. The sign will be negative or positive depending on the sign of δT.

In a paper published simultaneously with that of Hettner,[29] A. Einstein[30] treats in a qualitative but clear manner the theory of the action of the vane radiometer first made by Crookes. His considerations are as follows:

1. Take a body small compared with the mean free path placed in a gas space of large extent in which there exists a temperature gradient. The homogeneous temperature flux lies along the x-axis. All molecules are considered as having the same velocity u except for small differences representing the temperature gradient. It is further assumed that the molecules move only in the directions of the coordinate axes. The mean free path L is treated as a constant. This schematic representation of the gas will give results of the proper order of magnitude. Using more rigorous methods will cause only small changes in the value of a constant factor, as is the case with all refinements of kinetic-theory treatment.

Assume a surface element s whose size is small compared to L placed normal to the x-axis, and assume the absence of any mass

motion of the gas. Then exactly equal number of molecules pass through s per second in opposite directions equal to $\frac{1}{2}(\frac{1}{3}Nsu)$, where N is the number of molecules per cm^3. To account for the heat flow, the velocity of the molecules u_+ in the positive sense of the x-axis must be slightly greater than u and that of those on the negative side u_- slightly less than u. The heat flow sf through the surface is given by

$$sf = \frac{1}{6}Nsu\left(\frac{m}{2}u_+^2 - \frac{m}{2}u_-^2\right).$$

If one call $\frac{1}{2}mu^2 = \frac{3}{2}KT$, and if one assume that u_+ and u_- are appropriate to the temperatures existing at the place of their last collision (*i.e.*, at L cm away from s), then one has in place of the above expression

$$f = -\frac{N}{2}KLu\frac{dT}{dx},$$

for

$$\frac{1}{2}m(u_+^2 - u_-^2) = -\frac{3}{2}K\frac{dT}{dx}(2L).$$

In place of the surface area considered, let one now assume a small solid body of surface s. There will be more momentum given it per unit time from the positive side of the x-axis than from the negative side. Thus there will be an excess of momentum k in the direction of the positive x-axis. This is given by

$$k = \frac{1}{6}Nsu(mu_+ - mu_-).$$

If the impulse given due to the recoil of the impacting molecules is neglected, then k will also be the force on this surface. From this expression and the preceding one, the following equation results

$$k = \frac{sf}{u} = -\frac{1}{2}p\frac{L}{T}\frac{dT}{dx}s,$$

if it is assumed that u_+ and u_- are nearly equal to u, for

$$sf = -\frac{1}{6}Nsu\frac{m}{2}(u_+ - u_-)(u_+ + u_-)$$

$$= k\frac{(u_+ + u_-)}{2},$$

or

$$fs = ku,$$

where p is the gas pressure. The quantity f is, of course, only the heat flow due to translational velocity. To get the velocity

v of the particle the frictional force K' of the gas on the particle must be calculated. This force arises from the fact that the particle gives every molecule it strikes the impulse mv. A simple calculation gives this as follows: Call v the velocity of the particle, and m its mass. The molecule striking it from behind gives $2m(u - v)$ of momentum to the particle, the one striking from in front gives $-2m(u + v)$. The number of collisions from behind in unit time is $\frac{1}{6}Ns(u - v)$ and from in front is $\frac{1}{6}Ns(u + v)$. The net momentum transfer in unit time is

$$\frac{1}{6}Ns \cdot 2m[(u - v)^2 - (u + v)^2] = \frac{1}{3}Nsm[-4uv].$$

The resisting force K' is, therefore,

$$K' = -\frac{4}{3}Nsu(mv).$$

Equating k and $-K'$,

$$v = \frac{1}{4}\frac{f}{RT} = -\frac{1}{8}u\frac{L}{T}\frac{dT}{dx} = \frac{1}{4}\frac{f}{p}.$$

This velocity can be quite appreciable, and if the particle is small compared to L the velocity is independent of s as the equation shows. If L is 0.1 cm, $dT/dx = 30$, $T = 300°$, and in H_2 gas one obtains v of the order of 10^2 cm/sec. At atmospheric pressure this would be 0.1 mm/sec.

2. Consider next the effect of a small hole in a large thin partition placed normal to the heat flow. It is well known that in a vessel, even if its temperature is not uniform, there exists an equality of pressure. This holds as long as the dimensions considered are large compared to a free path as seen in Sec. 83. Thus if the small elements of the preceding paragraph had been replaced by a large plane normal to the temperature flow, even though a temperature difference existed on both sides, the pressures would be equal. Every molecule striking from the negative x-direction has a velocity u_n on striking and leaves with a velocity u in the direction of the negative x. ν_n such impacts occur per second per unit area. The quantities u_p, u, and ν_p are the corresponding quantities on the positive side of x. It is assumed that u, the velocity of recession, is the same in the positive and negative senses of x. The condition for equality of pressure is that the total pressure $p = m\nu_n(u + u_n) =$

$m\nu_p(u + u_p)$. Moreover, the heat flow must be the same on both sides of the plate, which is expressed by the equation

$$f = \frac{\nu_n m}{2}(u_n^2 - u^2) = \frac{\nu_p m}{2}(u^2 - u_p^2).$$

Dividing the second equation by the first,

$$\frac{2f}{p} = u_n - u = u - u_p.$$

If this be placed in the expression

$\frac{p}{m} = \nu_n(u + u_n) = \nu_p(u + u_p)$, and if $\frac{\nu_n + \nu_p}{2}$ be called ν and set equal to $\frac{Nu}{6}$, then $\frac{p}{m} = \nu_n\left(2u + \frac{2f}{p}\right)$ and $\frac{p}{m} = \nu_p\left(2u - \frac{2f}{p}\right)$. Whence

$$\nu_p - \nu_n = \frac{f}{up}(\nu_n + \nu_p) = \frac{Nf}{6p}.$$

If there were a minute hole of surface s in the plane, then $(\nu_p - \nu_n)s$ more molecules would pass through in the sense of decreasing x in unit time than in the other sense. Thus the hole would have a current of gas of velocity v given by $\nu_p - \nu_n = -Nv$ passing through it. From this equation and the preceding equation, therefore,

$$v = -\frac{1}{6}\frac{f}{p}.$$

Both these considerations belong really to the pressures in the Knudsen régime. They, however, furnish a clue to the problem of the radiometer at higher pressures, for consider a vane of area large compared to a free path but placed in a vessel whose dimensions are larger than that of the vane by many free paths. At some distance from the edge of the vane, equality of pressure will exist as deduced above. At some distance beyond the edge of the vane, if a temperature gradient exists, conditions will obtain in which a minute body would experience a force sf/u. At the edges of the vane a gradual transition will occur between the two conditions. The width of the zone where this occurs will have the dimensions of a free path L. There will thus be a force normal to the edge of the vane whose value per unit length of edge is given by

$$K = \frac{fL}{u} = -\frac{1}{2}p\frac{L^2}{T}\frac{dT}{dx}.$$

This will occur as long as the plate or vane is large compared to the free path.

Einstein carries this over to the case of the vane warmed on one side only. To get this expression from the equation above, one must convert dT/dx for the gas into ΔT, the difference of temperature on the two sides of the vane. On page 317 the relation between the energy transport through the gas and the temperature difference was given by Knudsen as $\Delta E = \epsilon \Delta p \Delta T$. In this case $\Delta E = K\frac{dT}{dx}$, where K is the heat conductivity. Baule[7] has evaluated $\frac{1}{\epsilon}$ as $\frac{1}{\epsilon} = \frac{2\sqrt{2\pi}}{n+4}\sqrt{\frac{MT}{R}}$, and Bleibaum[87] uses $K = \frac{15R\eta}{M}$, $\eta = 0.78Lp\sqrt{\frac{M}{RT}}$ (see page 363 as well). Putting these equations together, one has $\Delta T = BL\frac{dT}{dx}$, where B is a constant depending on the nature of the gas and the numerical values above. Placing this in Einstein's equation

$$K = -\frac{1}{2}p\frac{L^2}{T}\frac{dT}{dx} = -B'pL\frac{\Delta T}{T}.$$

Einstein himself does not give this transformation but merely gives the approximate equation $K = -pL\frac{\Delta T}{T}$ (setting $B' = 1$), as the force *per unit length of edge.*

It is seen that the equation predicts a force which will move the vane from the warm to the cold side. The force is not proportional to the area of the vane, but to the area of a strip along the edges one mean free path wide. Furthermore, in the radiometer heated on one side the force should be independent of pressure, for pL is a constant independent of pressure.

To test this out Marsh, Loeb, and Condon[37] made radiometers having vanes suspended from a quartz fiber. These vanes were so constructed that they had equal area moments about the suspension, but their edge moments were greater on one side than on the other. On illumination, such vanes *always deflected towards* the *side of greater edge moment.* The deflections were not in the ratio of the edge moments, however. Later investigation by Marsh[31] showed that this was due to the fact that the deflection is proportional to ΔT as well as to the edge moment. The side of the vane with the greater edge moment was, by measurement

of its temperature, found to be markedly cooler than the side with the smaller edge moment. This was in keeping with the cooling effect of the edges mentioned by Hettner and Czerny. Again, the deflection should be independent of the pressure. A fourfold increase of the deflection was observed from 0.4 to 0.04 mm. It was found that the quantity ΔT also increased by a factor of 3 for the same pressure change. As the accuracy of temperature measurement was not high, it is impossible to say whether or not all the change in deflection with change in pressure could not be ascribed to changes in ΔT. Finally, the equation given by Einstein, which is good in order of magnitude only, was checked by actual measurements of the forces on the suspension, and the values of p, L, ΔT, and T observed. The force was found to be 0.02 dyne per cm of edge at a pressure of 0.03 mm. The Einstein equation gave a force of 0.03 dyne per cm of edge at the same pressure and with the value of ΔT observed. This agreement is good considering the experimental uncertainties and the undetermined constant in the equation.

The field needs further careful experimental work under controlled conditions and with a knowledge of the temperatures involved. Work of this nature would help a great deal to guide further theoretical investigation.

The equation of Einstein was unfortunately deduced on a basis of reasoning which was not strictly accurate. This was shown by Sexl[83] for the case of a body of dimensions small compared to L in a temperature gradient. Einstein, page 375, wrote that

$$k = \frac{1}{6} N s u (m u_+ - m u_-).$$

Sexl points out that in a stationary state with a temperature gradient normal to the small particle, one cannot write the expression as above assuming $N = N_+ = N_-$, hence

$$k = \frac{1}{6} s (N_+ m u_+^2 - N_- m u_-^2) = 0,$$

for in this case the quantities $N_+/N_- = u_-^2/u_+^2$ in the body of the gas. This fact is not inconsistent with the observed radiometric forces as Sexl points out, for these arise when $K\frac{dT}{dx}$ are different on the two sides of S, *i.e.*, when there is a temperature

difference present. According to Bleibaum[87] and apparently to Sexl,[83,84] despite the difficulty mentioned, the reasoning of Einstein is in essence correct, for since pressure equality holds for surfaces large compared with L while in the space outside small particles suffer a radiometric force (whatever the origin), there is a radiometric edge effect along a strip of the dimension of L at the edges. This effect is further borne out by all the experiments such as those of Bleibaum,[87] and Marsh, Loeb, and Condon,[37] and Knudsen.[62] Bleibaum goes further and assigns to the single-vane radiometer an action based on the Einstein effect alone, while, as Hettner and Czerny[29,90] show, the action of the fixed vane-moving vane radiometer is determined by the surface streaming. Certainly, as shown by Hettner and Czerny[90] (page 369), the Osborne Reynolds forces definitely play a rôle in the case of a single vane. Both Hettner[58] and Knudsen[82] show diagrammatically how the Osborne Reynolds streaming can cause a radiometric action on the single-vane radiometer in an enclosed space, though it appears possible that these considerations will be modified by relative dimensions. It must be clearly stated that the Einstein effect and the one due to Osborne Reynolds streaming are different and must not be confused. The difference lies in the fact that, while the approximate equation of Einstein gives the force K *per unit length of edge* as $K = -B'pL\frac{\Delta T}{T}$, and hence the force on a vane of perimeter l as $R' = Kl = -B'plL\frac{\Delta T}{T}$, the exact equation of Sexl[84] for a circular disc or plate gives $R' = -\frac{14.72}{n+5}pL^2\frac{\Delta T}{T}$. Hence the Einstein effect is independent of pressure and depends on vane perimeter, while the Osborne Reynolds effect as deduced by Hettner[58] and Sexl is proportional to $1/p$ (since L is proportional to $1/p$) and is independent of the size of the disc. Dependence on edge length has indubitably been shown for larger vanes by several investigators, and pressure independence within the limitations of temperature variations has also been shown. The Hettner-Sexl equation has been checked only quantitatively for very small particles (about L in dimensions, *i.e.*, for photophoresis) and this only by use of a semi-empirical equation since in this region of dimensions an intermediate equation between the Knudsen equation and the Sexl equation could be applied. Bleibaum[87]

states her belief that at higher pressures than 10^{-2} mm of Hg the Osborne Reynolds phenomenon must play an important rôle, though more work must be done in this field to give a decisive answer. Knudsen,[62] as will later be seen, discusses the semi-empirical equation from the point of view of the edge effect. It is probable that both effects occur and that the predominance of one or the other depends on the material, size, shape, and surfaces of the vane, the dimensions of the gas space, and the method of heating.

Before taking up Knudsen's latest contribution, one or two more theories must be mentioned. One is due to Sterntal[85] which makes the radiometric effect at higher pressures an effect dependent on surface area. His equation utilizing the effect of the nature of the surface (accommodation coefficient) according to Bleibaum,[87] gives the pressure $P = \frac{R'}{A} = k'L\frac{p}{T}\frac{dT}{dx}$ in contradistinction to the Einstein law which reads $K = \frac{R'}{l} = k''L^2\frac{p}{T}\frac{dT}{dx}$. It has, however, been shown by Sexl[84] that the law of Sterntal violates the law of conservation of momentum and is therefore incorrect. In an abstract P. S. Epstein[86] gives two equations for a thin-circular-disc single-vane radiometer at pressures where the dimensions of the vane are $>>L$, whose derivation is not available. These equations give the radiometric forces R_1', and R_2' for the case of a vane with poor heat conduction (R_1') and one with good heat conduction (R_2') as

$$R_1' = -\frac{1.7a}{K_a}\frac{pL^2}{T}I \text{ and } R_2' = -\frac{2.66\delta}{K_i}\frac{pL^2}{T}I.$$

Here p, T, and L have the same meaning as before, while K_a is the heat conductivity of the gas, K_i that of the vane material, a is the disc radius, and δ is its thickness, while I is the radiant energy incident on unit area of surface. The equation for R_2', except for a slight difference in numerical constants, agrees with that of Sexl[84] (page 374). If the heat conductivity of sooted mica is considered poor, it is possible that the equation for R_1' will agree with the results of Marsh as it is proportional to the perimeter.[31] These equations merit experimental test.

Knudsen,[62] in his admirable paper on radiometric forces and accommodation coefficient, discusses the expression for the vane

radiometer at *low* pressures when two sides have different accommodation coefficients a_t' and a_t'' for translatory energy. In this case the vane is uniformly heated to a temperature T_1 above the gas and is isolated in space. He heats the vane which is conducting either electrically or by radiation. The pressure difference set up on the two sides at *low* pressures then is

$p' - p'' = \frac{p(T_1 - T_0)}{4T_0}(a_t' - a_t'')$, (page 322) when $T_1 - T_0$ is small,

where T_1 is the temperature of the vane or strip, T_0 that of the gas, and p' and p'' are the pressures on the sides of the vane having accommodation coefficients a_t' and a_t'', respectively. Thus, if a_t' is greater than a_t'', p' will be greater than p'', and the vane will move toward the side of lower accommodation coefficient. The motion in this case is opposite to that for the vane-plate radiometer blackened on one side, shown in Fig. 53. At higher pressures Westphal[28] found that log p plotted against $p' - p''$ gave a curve which is symmetrical about a maximum value (see page 372). This relation, as previously shown, demands that $p' - p'' = \frac{1}{\frac{1}{ap} + bp}$, where a and b are constants. Knudsen observed small but practically negligible deviations from Westphal's law so that he uses it. This gives a semi-empirical relation for the *general* radiometric equation good for all pressures, of the form

$$p' - p'' = \frac{\frac{1}{2}p\left(\sqrt{\frac{T_1}{T_0}} - 1\right)(a_t' - a_t'')}{1 + b_1 p + c_1 p^2}$$

which fits his observations in He and H_2 admirably. Here $a_t' - a_t''$ and the constants b_1 and c_1 vary very little with T_1. These experiments were carried on with a constant $T_1 - T_0$ which was maintained by heating the strip. Since the radiometer effect is an edge effect at higher pressures (at which $c_1 p^2$ predominates), c_1 must be proportional to the breadth B of the vane. (In Knudsen's case the vane was a long narrow strip.) Hence $c_1 = CB$. For small values of $T_1 - T_0$ the equation reduces to

$$\frac{p' - p''}{T_1 - T_0} = \frac{1}{4T_0}(a_t' - a_t'')\frac{1}{\sqrt{CB}}\frac{1}{\frac{1}{p\sqrt{CB}} + p\sqrt{CB} + \frac{b_1}{\sqrt{CB}}}.$$

If B is in cm, $\sqrt{C} = 0.0105$ for He and 0.0149 for H_2, while $b_1 = 0.00545$ for He and 0.00819 for H_2. The quantities b_1 and $\sqrt{CB}$ must have the dimensions of $1/p$. When $\sqrt{CB} = 1/p$, the forces have a maximum and

$$\left(\frac{p' - p''}{T_1 - T_0}\right)_M = \frac{1}{4T_0}(a_t' - a_t'')\frac{1}{\sqrt{CB}}\frac{1}{2 + \frac{b_1}{\sqrt{CB}}}.$$

Experimentally b_1 is nearly $\sqrt{CB}$. Setting $b_1 = \sqrt{CB}$, one obtains

$$\left(\frac{p' - p''}{T_1 - T_0}\right)_M = \frac{1}{12T_0}(a_t' - a_t'')\frac{1}{\sqrt{CB}}.$$

Thus to get the maximum forces for a given area, B must be made small by cutting the area into strips.

This study of the radiometric forces differs from the preceding cases as it maintains a constant body temperature and measures forces due to edge effect and accommodation coefficient. Hence in this case the maximum is reached at higher pressures than for the case where the vane is illuminated by a radiant source. In the present case $T_1 - T_0$ is maintained constant, while, as p varies with the irradiated vane due to changing gas conduction, $T_1 - T_0$ decreases rapidly, thus bringing the maximum effect at lower pressures. Knudsen[80] analyzed the gas motion in the case of the strip placed along the axis of a cylindrical tube. The blackened side with a higher a_t', and thus an equivalent higher gas temperature adjoining it, causes a streaming from the cold side a_t'' to the warmer side. Hence the streaming causes a reaction on the vane from the blackened side to the polished side. It acts as if the gas on the blackened side had a higher temperature and hence higher pressure than that on the polished side. The narrower the tube and hence the less space for equalization, the greater the pressure should be. Hence for this type of reaction it is clear that the *exact* equations must contain terms involving the shape and dimensions of the container. Knudsen attempted to find a relation between radiometric force and the energy emission from the two sides of the heated strip. The results were quite complicated and no satisfactory relations were established.

Knudsen then constructed a torsion balance. On one side there was a long narrow strip of Pt with the front blackened and

the rear polished. On the other arm the system consisted of two strips of Pt with polished sides towards each other and separated by thin glass strips. The front side of this double vane was blackened and the other side was polished. Each strip could be illuminated separately from either polished or blackened side. With this arrangement the single strip being a good conductor allowed of a comparison of the effects produced by the difference in accommodation coefficients alone, when illuminated. Illumination on both sides of the single strip produced deflections *away* from the blackened side, the one with the blackened side illuminated being the greater as T_1, the vane temperature, was greater in this case in virtue of greater absorption. This effect is clearly explained as due to a difference in the accommodation coefficients as the temperature was sensibly the same on both sides of the strip.

In the case of the double vane, the effects were such that at *low* pressures the illuminated side was always repelled. This simply meant that, while accommodation coefficients played some rôle, the higher temperature of the illuminated side produced an effect which preponderated over that due to difference in accommodation coefficients. The force on the double vane at low pressures when the blackened side was illuminated was four times that of the single vane so illuminated, thus showing directly the effect of temperature difference. At *high* pressures the force on the double vane was away from the blackened side on illumination of either side in the same fashion as for the *single vane at all pressures*. Under these conditions, the higher gas pressure increased gaseous conduction between the two sides of the double vane so that the temperatures on the two sides equalized and the side with the higher accommodation coefficient experienced the greater force. At very high pressures the forces on single and double vane were nearly equal with either side illuminated. When air with a low heat conductivity replaced the H_2 gas used above, analogous results were obtained, except that at high pressures the double vane always showed greater forces than the single vane. When the double vane was illuminated on the polished side, the force was always away from the source of illumination since the blackened side never reached the temperature of the illuminated side, owing to poor conduction between them in air, even at higher temperatures. Knudsen also used two strips of the same length and thickness, one being

one-half the width of the other. The force on the narrow and broad vane was the same at higher pressures, showing the edge effect quite clearly. This equality held from 33.5 mm of Hg to about 1 mm. Below this pressure the broad strip began to show the effect of its greater area (the wider strip was 3 mm wide, 45 mm long; the other had the same length but was 1.5 mm wide, and both were 0.0026 mm thick). At very low pressures, *i.e.*, in the Knudsen régime, the force on the broader strip was about twice as great as on the narrower strip.

The result of Knudsen's investigations thus adds the following important facts to the knowledge concerning the nature of radiometric forces at higher pressures. The force is again shown to depend on the edge length and not on the area, until the pressures are such as to bring one to the Knudsen régime in which the area is the determining factor. The effect is shown to depend on a real or effective difference of temperature of the two sides, the forces being such as to cause the force on the warmer side to predominate. A vane with different accommodation coefficients on the two sides but having sensibly the same temperature on both sides will cause the side with the larger coefficient to have the greater force exerted on it, just as if it were the warmer side. This force, due to a difference in the value of the coefficient on the two sides of the vane, is of appreciable magnitude even at the higher pressures. The gaseous-heat conductivity can play an important rôle in altering the temperatures of the sides of the vanes in cases where the heat conductivity of the vane material is low. These facts must be considered in any investigation of the nature of the radiometric forces at different pressures.

One may then summarize the results of the investigation of the action of the vane radiometer at higher pressures as follows. The effect is an edge effect in part of the Osborne Reynolds type and in part of the Einstein type. The predominance of one type over the other doubtless depends on the particular disposition of the vane and adjacent surfaces in the gas space, as well as material and construction of the vane, and at present no exact general and comprehensive single theory of the phenomenon exists, although theories applicable to either phenomenon and special cases have been derived. In this direction much more experimental study is needed. In the discussion of these forces it is essential that the temperature distribution

over the vane surface be known and that the cooling effect of the edges be studied. The heat conductivity of the vane and the gas must be taken into account so that the temperature differences on the two sides of the vane, calling forth a radiometric force, be known. This difference is also influenced by the thickness of the vane. Finally, the effect of a difference of accommodation coefficients on the two sides of the vane calling forth a radiometric effect of its own must be recognized and must be included in the calculations. It is seen therefore that the problem is a complicated one which, although understood qualitatively, requires much more investigation experimentally to permit a satisfactory theory to be developed.

References

1. Poisseuille, J. L. M.: See reference 8, Chap. VI, part I.
2. Kundt and Warburg: *Phil. Mag.*, **50,** 53, 1875; *Pogg. Ann.*, **155,** 337, 525, 1875.
3. Maxwell, J. C.: "Scientific Papers," vol. 2, p. 708.
4. Knudsen, M.: See Secs. 77, 78, 79, 80, 81, 82 for references.
5. Langmuir, I.: See references 39, 40, 41.
6. Dunnoyer: "Popular Lectures," Société Française de Physique, Ser. 2, p. 214, Gauthier-Villars, Paris, 1913.
7. Baule: *Ann. Physik*, **44,** 145, 1914.
8. Blankenstein: *Phys. Rev.*, **22,** 582, 1923.
9. Van Dyke, K. S.: *Phys. Rev.*, **21,** 250, 1923.
10. Stacy, J. L.: *Phys. Rev.*, **21,** 239, 1923.
11. Knudsen, M.: *Ann. Physik*, **28,** 75, 1909.
12. Knudsen, M.: *Ann. Physik*, **28,** 999, 1909.
13. Von Smoluchowski: *Wied. Ann.*, **64,** 101, 1898.
14. Knudsen, M.: *Ann. Physik*, **32,** 809, 1910.
15. Soddy and Berry: *Proc. Roy. Soc.*, **A83,** 254, 1910.
16. Knudsen, M.: *Ann. Physik*, **34,** 593, 1911.
17. Von Smoluchowski: *Ann. Physik*, **35,** 983, 1911.
18. Von Smoluchowski: *Sitzb. Akad. Wiss. Wien*, **107,** 19, 1898, **107,** 304, 1898.
19. Maxwell, J. C.: *Phil. Trans. Roy. Soc.*, p. 332, 1879.
20. Von Smoluchowski: *Ann. Physik*, **35,** 1006, 1911.
21. Knudsen, M.: *Ann. Physik*, **31,** 205, 1910; **33,** 1435, 1910.
22. Reynolds, Osborne: See Maxwell: "Scientific Papers," vol. 2, p. 708.
23. Stoney, G. J.: *Sci. Trans. Roy. Soc. Dublin*, **1** (2), 39, 1878.
24. Fitzgerald: *Phil. Mag.*, **7,** 15, 1879.
25. Gerlach and Westphal: *Verh. d. Deut. Phys. Ges.*, **21,** 218, 1919.
26. Westphal: *Z. Physik*, **1,** 92, 1920.
27. Gerlach: *Z. Physik*, **2,** 207, 1920.
28. Westphal: *Verh. d. Deut. Phys. Ges.*, **21,** 129, 1919.
29. Hettner and Czerny: *Z. Physik*, **27,** 12, 1924.

30. Einstein, A.: *Z. Physik*, **27**, 1, 1924.
31. Marsh, H. E.: *J. Optical Soc. Am.*, **12**, 135, 1926.
32. Einstein, Edith: *Ann. Physik*, **69**, 241, 1922.
33. Maxwell: *Phil. Trans. Roy. Soc.*, **170**, 1, 231, 249, 1879.
34. Rubens and Nichols: *Wied. Ann.*, **60**, 401, 1897.
35. Nichols: *Astrophys. J.*, **13**, 104, 1901.
36. Westphal: *Z. Physik*, **1**, 92, 431, 1920; **4**, 221, 1921
37. Marsh, Loeb, and Condon: *J. Optical Soc. Am.*, **11**, 257, 1925.
38. Wood, R. W.: *Phil. Mag.*, **30**, 300, 1915; **32**, 364, 1916.
39. Langmuir, I.: *Phys. Rev.*, **8**, 149, 1916.
40. Langmuir: *J. Am. Chem. Soc.*, **40**, 1361, 1918.
41. Langmuir: *Trans. Faraday Soc.*, **17**, Part III, 1921.
42. Knudsen, M.: *Ann. Physik*, **50**, 472, 1916.
43. Frenkel: *Z. Physik*, **26**, 117, 1924.
44. Dunnoyer: *Compt. Rend.*, **152**, 593, 1911.
45. Chariton and Semenov: *Z. Physik*, **25**, 287, 1924.
46. Weyssenhoff: *Ann. Physik*, **58**, 505, 1920.
47. Langmuir, I.: *Trans. Faraday Soc.*, **17**, Part III, p. 7, 1921.
48. Soddy and Berry: *Proc. Roy. Soc.*, **84**, 576, 1911.
49. States, M. N.: *Phys. Rev.*, **21**, 662, 1923.
50. Gaede: *Ann. Physik*, **41**, 289, 1911.
51. Millikan, R. A.: *Phys. Rev.*, **21**, 217, 1923.
52. Epstein, P. S.: *Phys. Rev.*, **23**, 710, 1924.
53. Andrén: *Ann. Physik*, **42**, 1, 1917.
54. Barus, C.: *Phys. Rev.*, **22**, 1906.
55. Kammerlingh-Onnes *Arch. Néerland. Sci.*, **30**, 113, 1897.
56. Langmuir, I.: *Proc. Nat. Acad. Sci.*, **3**, 141, 1917.
57. Jellinek, K.: "Lehrbuch der Physikalischen Chemie," vol. 2, p. 240, F. Enke, Stuttgart, 1914.
58. Hettner, G.: *Z. Physik*, **37**, 179, 1926.
59. Fraser, R. G. J.: "Molecular Rays," Cambridge University Press, Cambridge, 1931.
60. Lorentz, H. A.: "Lectures on Theoretical Physics," vol. 1, Chap. III, Macmillan & Co., Ltd., London, 1927.
61. Clausing, P.: *Z. Physik*, **66**, 471, 1930; *Ann. Physik*, **12**, 961, 1932; *Physica*, **9**, 65, 1929.
62. Knudsen, M.: *Ann. Physik*, **6**, 129, 1930.
63. Cockcroft, J. O.: *Proc. Roy. Soc.*, **A119**, 293, 1928.
64. Wertenstein: *Jour. Physique*, **4**, 281, 1923.
65. Clausing, P.: *Ann. Physik*, **7**, 489, 521, 569, 1930.
66. Zener, C.: *Phys. Rev.*, **40**, 335, 1932.
67. Roberts, J. K.: *Proc. Roy. Soc.*, **A135**, 192, 1932; **A129**, 146, 1930.
68. Knudsen, M.: *Ann. Physik*, **48**, 1113, 1915.
69. Gaede: *Ann. Physik*, **41**, 331, 1913.
70. Epstein, P.: *Phys. Rev.*, **23**, 710, 1924. Clausing, P.: *Ann. Physik*, **4**, 533, 1930.
71. Taylor: *Phys. Rev.*, **35**, 375, 1930.
72. Ellett and Olson: *Phys. Rev.*, **31**, 643, 1928.
73. Ellett, Olson, and Zahl: *Phys. Rev.*, **34**, 493, 1929. Zahl: *Phys. Rev.*, **36**, 893, 1930.

74. Johnson, T. H.: *Jour. Franklin Inst.*, **206,** 301, 1928; **207,** 639, 1929; **210,** 135, 1930. Johnson, T. H.: *Phys. Rev.*, **35,** 1299, 1930.
75. Knauer and Stern: *Z. Physik*, **53,** 779, 1929. Estermann and Stern: *Z. Physik*, **61,** 114, 1930. Estermann, Frisch, and Stern: *Z. Physik*, **73,** 348, 1931.
76. Zener, C.: *Phys. Rev.*, **40,** 178, 1932.
77. Volmer and Estermann: *Z. Physik*, **7,** 1, 13, 1921. Volmer and Adhikari: *Z. Physik*, **35,** 170, 1925; *Z. Phys. Chem.*, **119,** 46, 1926. Volmer, G.: *Z. Phys. Chem.*, **115,** 253, 1925.
78. Hückel, E.: "Adsorption und Kapillarkondensation," pp. 153–177, Leipzig, 1928. Jaquet, E.: Theory of Gaseous Adsorption, *Fortschritte Chemie, Physik und Phys. Chem.*, vol. 18, no. 7, Berlin, 1925.
79. Clausing, P.: *Physica*, **6,** 48, 1926; **8,** 289, 1928.
80. Becker: *Phys. Rev.*, **28,** 341, 1926.
81. Knudsen, M.: *Ann. Physik*, **83,** 797, 1927.
82. Knudsen, M.: *Ann. Physik*, **6,** 172, 1930.
83. Sexl, Th.: *Ann. Physik*, **81,** 801, 1926.
84. Sexl, Th.: *Z. Physik*, **52,** 249, 1929.
85. Sterntal, A.: *Z. Physik*, **39,** 341, 1926.
86. Epstein, P.: *Phys. Rev.*, **31,** 914, 1928.
87. Bleibaum, Irma: *Z. Physik*, **49,** 590, 1928.
88. Mattauch, J.: *Ann. Physik*, **85,** 967, 1928.
89. Ehrenhaft, F.: *Ann. Physik*, **56,** 81, 1918.
90. Hettner and Czerny: *Z. Physik*, **30,** 258, 1924.

Books Recommended

a. Dunnoyer: *Loc. cit.*, Ser. 2, p. 214.
b. Bloch, E.: "Kinetic Theory of Gases," Chap. IX, translated by P. A. Smith; Methuen & Co., London, 1924.
c. Dunnoyer, "High Vacuum Practice," D. Van Nostrand & Co., New York, 1926.
d. Hertzfeld, K. F.: "Kinetische Theorie der Wärme," Müller-Pouillet's "Lehrbuch der Physik," vol. 3, part II, Chap. Iβ, Secs. 17–31, F. Vieweg und Sohn, Braunschweig, 1925.
e. Fraser, R. G. J.: "Molecular Rays," Cambridge University Press, Cambridge, 1931.

CHAPTER VIII

THE REALITY OF MOLECULAR MOTIONS, BROWNIAN MOVEMENTS

85. Introduction.—In the preceding seven chapters the kinetic concept of a gas and its consequences was developed in some detail, and the development in many cases resulted in predictions which were more or less successfully verified by experiment. Thus in more recent years the predicted velocities of silver atoms, the distribution of velocities, and free paths were directly measured and found to be in agreement with the theory. Furthermore, the representation of the various constants of transfer discussed in Chap. VI in terms of the kinetic theory at an early date furnished strong indications of the correctness of the assumptions of the kinetic hypothesis. However, while these predictions were fulfilled, until 1908 no direct proof of the fundamental assumption of the kinetic theory existed; to wit, no proof of the continuous and eternal heat motions of the molecules was known. To place the kinetic hypothesis on the basis of a proper theory, such a proof was absolutely essential, and it was due to the lack of this evidence that the proponents of the school of energetics (see Chap. I) had a legitimate foundation for their criticism of the kinetic conception of gases.

Again, before 1908, there was no direct means of estimating the Avogadro or Loschmidt's number N, that is, the number of molecules in a gram-molecule or in a cm^3. It is true that the quantities N and σ, the molecular radius, were bound together in the equation for the mean free path, $L = \frac{1}{\sqrt{2}\pi\sigma^2 N}$, and it is clear that if σ could be evaluated N could be determined. Previous to this date attempts had been made to evaluate σ from the limiting thickness of soap-solution films just before they break[1] (*i.e.*, where the film was supposed to be two molecules thick), and from the value of Van der Waals' b.[1] The first method gave very crude and uncertain results of the order of ten times the value of σ obtained from b taken from the critical data. Clearly then, it

remained for a direct determination of N, and a direct proof of the heat motions of the molecules to establish the kinetic hypothesis on the firm basis of an acceptable theory.

These conditions were realized at one stroke through the genius of the French physical chemist, Jean Perrin,[2] in 1908, by a study of the Brownian movements. By means of these movements by two independent lines of reasoning, based on the assumptions that they were the result of molecular motions, Perrin was able to obtain a value of N in good agreement with the value of N calculated from σ from the critical data. The value of N thus obtained was also in satisfactory general agreement with the early rough values of N obtained by Millikan[3] and Rutherford[4] from Ne and the value of e the unit electric charge by entirely different means. The agreement of observations on the Brownian movements with the equations derived, assuming them to be the result of molecular impacts, definitely established the real existence of the assumed heat motions. Later experiments of Millikan and Fletcher[5] using minute electrically charged oil drops in air giving an accurate value of the Faraday constant Ne verified the assumptions in a still more striking manner. The theory and the results of these measurements will constitute the body of this chapter.

86. Brownian Movements.—In 1827, an English botanist, Brown, observed that in aqueous suspensions of fine inanimate spores the spores were apparently in constant motion dancing hither and thither in the field of the microscope without apparent rhyme or reason. He extended his observations to suspensions of a large number of inorganic substances, the so-called colloidal solutions, and found it to be a general phenomenon. His observation of the motions led him to venture the idea that the motion was due to the unequal bombardment of the particles on various sides by the molecules of the liquid executing their heat motions and that they were therefore a manifestation of molecular heat motions. This started a violent controversy and a long line of experimental investigations by now nearly unknown investigators which definitely terminated only with the quantitative experiments of Perrin. The investigations preceding the work of Perrin established the following facts, which in a qualitative fashion pointed quite strongly to the correctness of the tentative explanation of Brown. These facts are as follows:

1. The motions are completely irregular and random. No two particles in one locality are moving in the same direction at the

same time. The motions are also independent of the location of the particles in the observation chamber. Thus they cannot be due to eddy, convection, or streaming motions in the liquid.

2. They are independent of jarring or shaking of the vessel.
3. The lower the viscosity of the liquid the faster the motion.
4. The smaller the particles the greater the motion.
5. Two particles the same size move equally fast at the same temperature.
6. The motions are continuous and eternal, that is, the colloidal quartz particles in the liquid suspensions included in certain quartz specimens that are thousands of years old still show the Brownian movements. Thus these cannot be attributed to special types of physical activity, such as is displayed by camphor on a clean water surface, for such actions cease after a short interval of time.

These results indicate first that the motions are properties of individual particles, that each one of these acts independently, and that local convection currents, streaming, and mechanical agitation are not the cause of them. The variation of the motion with size, viscosity, and temperature is in agreement with the concept that they are due to unbalanced forces of the molecular type. Finally, the eternal nature of the motion suggests that the energy cannot come from the chemical or electrical properties of the suspension and the only source of energy of this duration is the ever-present heat motion of the liquid molecules.

Accepting Brown's hypothesis then, the following picture of the processes at work may be drawn. The suspended particles, large compared to the molecules of the liquid (perhaps millions of times larger) are being continually bombarded on all sides by molecules of the liquid executing their heat motions. If the particles are sufficiently large, on the average, equal numbers of molecules strike them on all sides each instant. For smaller particles, from the laws of chance, the numbers striking various sides each instant may not be equal. Thus the particle at each instant suffers an unbalanced force due to the inequality in the number of molecular impacts on different parts of the surface. The result of such an action is a force causing the particle each instant to move this way or that in response to the force, its motion being opposed by the viscous drag of the liquid. Thus the particles act just like very large molecules in the liquid and the motions they exhibit should be exactly analogous to the real motions of the molecules.

It is the similarity of these large observable particles to molecules that Perrin used as the basis of one of his proofs, for if these particles differ from molecules in their behavior in respect to heat motions just in size, they should obey the laws of partial pressures and of molecular atmospheres. Also if the particles are moved hither and thither by the unbalanced forces of the liquid, the mathematical theory of the amplitude of their motion in a given time for particles acted on in the fashion deduced by von Smoluchowski and later independently by Einstein should be applicable to this case, and the dependence of the amplitude on various factors, such as temperature, size, and viscosity, should be in accord with that observed. The test of this equation constitutes the second of Perrin's methods of attack and it will be the task of the next two sections to derive the relations and indicate the success of the measurements.

87. Brownian Movements and the Law of Atmospheres.— The study of the physical chemistry of solutions has shown that molecules of dissolved substances in a liquid behave in many respects as if the same molecules were moving freely as gas molecules in empty space. Thus the molecules of 342 grams (*i.e.*, 1 gram-molecule), of cane sugar dissolved in 22.4 liters of solution act very much as if they were molecules of sugar vapor at a pressure of 1 atmosphere at the existing temperature, that is, they execute heat motions and exert a partial pressure on the walls, commonly known as the osmotic pressure. By using heavier molecules than sugar, the case is not altered, for there is no change in the observed laws with molecular weight. There is no reason why the molecules to be discussed, even if they have the size of colloidal protein molecules visible as diffraction patterns in the ultra-microscope, should not show exactly the same behavior as sugar solutions of low molecular weight.[17]* It is, therefore, not

* It appears now that, in spite of the views of certain colloidal chemists, colloidal particles in suspension do not differ essentially from crystalloidal particles in solution. Their chief difference lies in their greater size, which makes them unable to pass through certain filters and which also enables them to scatter light. They are also at times electrically charged, the charge being very active in preventing agglomeration and precipitation. Certain crystalloidal solutes (the ions), however, also exhibit charges in solution whose nature may not be very different from that of the particles above. They also follow the laws of osmotic pressure. It is possible that the charges on Perrin's particles might have affected his results. Apparently, he chose particles where this was not the case. That he did so is evidenced by results of later workers who could not check *some* of his results.

unlikely that the laws of solutions and hence of gases are justifiably applicable to suspensions of colloidal particles in liquids. It was this analogy which lead Perrin to the first of his considerations.

Assuming that the colloidal particles in a suspension may be compared to an atmosphere of molecules in free space, say the nitrogen molecules of the atmosphere, it is possible to proceed as follows. The nitrogen molecules of the earth's atmosphere are in constant heat motion. Due to this, they are moving equally in all directions. At the same time they are acted on by gravity. Accordingly, those in the outer layers have a resultant force urging them towards the center of the earth, that is, there is a pressure exerted by them on the next inner layer of molecules. These, in turn, are attracted inwards, and they add the force of attraction upon themselves to the pressure exerted on them by the outer layer. Through their heat motions the pressure is transmitted from layer to layer of the gas, becoming continually greater as the center of the earth is approached. Since the pressure acting from above increases the density of the gas, more molecules are crowded into each successive layer than there were in the layer before. Hence the attractive force on an inner layer will be greater than on the next outer one and the pressure will increase more rapidly than by a linear law with the decrease in distance from the center. Also, the heavier the gas molecules the greater the gravitational force on each layer, and hence the more rapidly the pressure will increase with decreasing distance from the center. Thus for nitrogen there is an atmosphere like that of the earth—tenuous outside, dense at the surface. For molecules like sugar that are some 10 times heavier than nitrogen it would be necessary only to go up a distance $\frac{1}{10}$ as high to reach the same fractional density as is exhibited by the atmosphere. For colloidal particles whose mass may be 10^6 times that of the sugar molecules the fractional change in density, which in the atmosphere requires kilometers in height, will occur in millimeters in colloidal suspensions. Thus if the colloidal particles showing Brownian movements act exactly as if they were large molecules, their motions being due to the heat motions of the molecules of the liquid, a colloidal suspension should show a change in density for different layers depending on the mass of the particles, but exactly analogous in form to the changes in density of the earth's atmosphere. To study this, the law of atmospheres, which was originally due to Laplace, must be deduced.

Consider a cylinder of gas of cross-section a and also one of the layers mentioned above dh cm high. Call the pressures on its bottom and top p and p'. Then $p > p'$, for the mass of the layer dh acted on by gravity has been added to p' to make p. Thus $p - p' = \frac{(a)(dh)\rho g}{a}$. This merely says that the force of gravity $a\,dh\rho g$ acting on the gas divided by the area a is the difference in pressure $p - p'$. Here g is the constant of gravity and ρ is the density of the gas in grams per cm^3. Hence

$$dp = p - p' = -dh\rho g = -\frac{Mgdh}{v},$$

the minus sign indicating that as h increases p decreases. Here M is the mass of a gram-molecule of gas, and v the corresponding volume $\left(i.e., \rho = \frac{M}{v}\right)$. Since it was assumed that the Brownian particles act like nitrogen molecules, it is legitimate in the rough calculations to follow to assume that Boyle's law holds. Then for such particles as for N_2 one may approximately write $pv = R_AT$, where v and R_A refer to a mol, and one has

$$dp = -\frac{Mgdh}{\frac{R_AT}{p}}$$

or

$$\frac{dp}{p} = -\frac{Mg}{R_AT}\,dh.$$

Integrating this from $p = p_0$ at $h = 0$, to $p = p$ at $h = h$,

$$\int_{p_0}^{p}\frac{dp}{p} = -\frac{Mg}{R_AT}\int_0^h dh, \quad \log p - \log p_o = -\frac{Mg}{R_AT}\,h$$

$$p = p_o e^{-\frac{Mg}{R_AT}h}.$$

Further, since the number of particles or molecules per cm^3, n_o and n, are proportional to p_o and p, respectively,

$$n = n_o e^{-\frac{Mg}{R_AT}h}.$$

This is Laplace's well-known law of atmospheres and it expresses precisely how the number of particles or molecules per unit volume will vary with distance from the earth's surface.* The

* This law is also a consequence of the law of equipartition of energy (see p. 93).

equation may be modified a bit further by replacing M, the gram-molecular mass, by mN_A, the mass of a single particle times the number in a gram-molecule, hence

$$\frac{n}{n_o} = e^{-\frac{mN_A gh}{R_A T}}.$$

Thus the density of particles increases exponentially as the height decreases. The rate of increase is greater the greater the mass m of the particles, and the lower the temperature. If the values of m, g, h, R, and T were known for a given $\frac{n}{n_o}$ and h, N_A, the Avogadro number, could be found.

In the colloidal particles in solution the force of gravity acts on the particles which are buoyed up by the liquid in which they are suspended. Thus mg must be replaced by $m\left(\frac{D-d}{D}\right)g$, where d is the density of the liquid and D is the density of the particles. If V is the volume of the particles, then

$$\frac{n}{n_o} = e^{-\frac{N_A}{R_A T}m\left(1-\frac{d}{D}\right)gh}$$

$$= e^{-\frac{N_A}{R_A T}V(D-d)gh}.$$

In the logarithmic form this becomes

$$\log\frac{n_o}{n} = \frac{N_A}{R_A T}V(D-d)gh.$$

To test this experimentally, Perrin used colloidal suspensions of gum mastic and of gum gamboge. These could be prepared by dissolving the gum in alcohol and then pouring the clear solution into water. In this way clear spherical globules of the substances appeared, of which the smaller ones showed the Brownian movements very nicely. The equation to be tested, however, demands the V or m for all the particles considered be the same. To insure this, Perrin separated particles of one size from the assorted groups present in the initial emulsion by fractional centrifuging. These were then placed in small cells kept at constant temperatures by water baths and placed on the stage of the microscope. Since the depth of focus of a microscope is very sharp, the number of particles in the field F of the microscope and of a

depth dh could be easily counted. By raising or lowering the microscope, the numbers n at different levels in the volume Fdh could be counted at different depths. The value of h for different settings of the microscope yielding a number n could be read accurately from the graduated head of the adjusting screws of the microscope governing its distance from the solution. Thus n_o, n, and h starting at some arbitrary depth in the solution could be determined. The counting of moving particles in the field was difficult, due to the motions. This was overcome by reducing the field so that about 10 particles appeared at one time. Perrin then counted the number in the field (the bursts of 0 to 10 particles) at various successive intervals of time. By averaging a large number of counts and knowing the area of the field of the diaphragm, he was able to arrive at a fairly accurate value of n.

The most serious difficulty in the measurements lay in an evaluation of m or V, and D. D was determined in three ways: (1) by the use of the pycnometer; (2) by direct measurement of the density of the fused dry gum; (3) by adding KBr, or a salt of known composition, to the solution to increase the density of the liquid until the density of the suspending liquid was so near that of the particles that violent centrifuging would not separate the particles.

1. The pycnometer method consisted in filling the pycnometer first with distilled water, and then with the suspension at the same temperature, and weighing it. The emulsion was next evaporated to dryness and the resin desiccated at 110°C. and weighed. The dry weight gave the mass of the gum particles present. The difference in the weight of liquid and distilled water gave the excess in mass of all the particles in the suspension over the water which they displace.

2. Unless the process of suspension changes the density of the gum, the density of the dried extracted gum should be the same as that of the particles.

3. The separation of particles by centrifuging, that is, by using powerful centrifugal forces, depends on the fact that the particles or substance of greater density will be thrown outward relatively more than the less dense substance (*i.e.*, the substance of less inertia, the solution). If the densities are the same, separation should be impossible. The precision of this method depends on the centrifugal forces being great enough to separate

particles of small enough differences in density to a noticeable extent in the time intervals used. It also demands that the salt added does not affect the nature of the suspension by causing agglomeration or change of constitution.

The results of the measurements by the three methods on the same suspension for one case are given by Perrin as $D_1 = 1.1942$, $D_2 = 1.194$, $D_3 = 1.195$.

The next problem was the accurate determination of m or V for the particles. The particles appeared as spheres, but the edges were not sharply defined, owing to the diffraction effects. Thus it was impossible to measure the diameter of any one accurately. It happens that if a very dilute suspension be evaporated on an uncovered microscope object glass the capillary forces of the liquid cause the particles to run together in groups. These groups are, in general, one particle in depth and may lie more or less in horizontal rows, or in sheets. Thus the diameter can be found by counting the number in a given area or the number lying side by side in a given straight row. As an example, Perrin found the diameter to be 0.746×10^{-3} mm for the average of 50 rows of from six to seven particles, and 0.738×10^{-3} mm for 2000 particles distributed over 10^{-5} cm^2. Thus if the diameter is known, V can be computed, assuming the particles spherical, and m can be found from D and V. Another way in which the mass of the grains can be found is by direct weighing. In slightly acid solution ($\frac{1}{100}$ normal), while the grains do not adhere to each other, they all adhere to the walls on striking them. Hence, after some hours all the particles are precipitated on the glass walls of the vessel. Thus, by precipitating the grains in this fashion on the walls of small cylinders whose volume could be measured, and by counting the number of grains so precipitated at various parts of the cylinder, a close estimate of the number of grains in the whole small volume of solution was obtained. By then evaporating a known volume of solution, the weight of the particles present could be determined. Thus by dividing the weight so obtained by the number of particles in this volume, deduced by the counting, the mass m of a single particle was determined. A third method of determining the radius of the particles made use of Stokes' law. Stokes has shown mathematically that for spheres moving through a viscous liquid under the action of uniform force, when the spheres are small compared to the diameter of the vessel but large compared

to the discrete structure of the liquid,* the velocity of fall is given by

$$v = \frac{V(D - d)g}{6\pi\eta a} = \frac{\frac{4}{3}\pi a^3(D - d)g}{6\pi\eta a},$$

where a is the radius of the sphere, v the velocity of fall, and η the coefficient of viscosity. This law holds for macroscopic spheres and for microscopic spheres, *if they are not too small.* If v, the velocity of fall of a cloud of suspended particles down a capillary tube, be observed in a liquid (distilled water) for which η is known, a can at once be found. Using these three methods, Perrin found the following values for a from a single emulsion.

	Alignment	Weight	Stokes' Law
a.....	0.371×10^{-4} cm	0.3667×10^{-4} cm	0.3675×10^{-4} cm

With these data then, it was possible to get N_A, for $\frac{n}{n_o}$ and h were observed, while m or V, D, and d were measured and R_A and T were known.

Before computing N_A, however, it was essential to know whether the equation between $\frac{n}{n_o}$, h, m, and T was verified.† This was found to be the case. The results obtained by Perrin in two typical experiments are as follows:

1. Particles of radius 0.212×10^{-4} cm, with 13,000 particles counted at depths of 5×10^{-4}, 35×10^{-4}, 65×10^{-4}, and 95×10^{-4} cm gave $\frac{n}{n_o}$ proportional to 100, 47, 22.6, and 12. Had these accurately followed the exponential law, they would have given 100, 48, 23, and 11.1.

2. In another series of experiments the particles were photographed in a plane normal to the earth's gravitational field and the numbers of particles at various levels were counted on the photograph. These particles had radii 0.52×10^{-4} cm and the distance between the levels was 6×10^{-4} cm. The numbers found for four levels were 1880, 940, 530, and 305. The exponential law leads one to expect 1880, 995, 528, and 280. The

* This assumption demands conditions which are the reverse of those for which the Brownian motions become noticeable. It is to this circumstance that part of the discrepancy between Millikan's result and that of Perrin is ascribed.[17]

† The question as to why particles can remain suspended and in motion in the gravitational force field often arises. The answer lies in the fact that the energy of agitation kT is greater than the potential energy mgh due to the forces (see p. 93).

deviations are all within the limits of probable variation for the numbers counted. Counts were made on suspensions of different sorts, η varying in a ratio of 1 to 125. T was varied from -9 to $+60$°C., while the volume V varied in the ratio of 1 to 50. These suspensions all obeyed the exponential law and led to values for the constant term which yielded a value of N_A lying between 6.5×10^{23} and 7.2×10^{23}. In these values there was no systematic variation of N_A with any factor. It can be safely assumed that the constancy of N_A and the verification of the exponential ratio confirm the assumptions involved in the deduction of the equation beyond a reasonable doubt.

88. The Displacement of the Particles in a Given Time and the Verification of the Brownian-movement Law of Einstein and von Smoluchowski.—The most striking proof of the molecular origin of the Brownian movements lies in the quantitative agreement of the displacements measured in a given time with the predicted value of the displacement based on the theory of Einstein[6] and von Smoluchowski.[7] As was stated, the particles are acted on each instant by unbalanced forces due to unequal molecular bombardment on various sides. The force opposing this motion is the viscous drag of the liquid. As a result of this, the particles move hither and thither through the liquid. If one particle be observed in the field of the microscope which has a series of lines cutting each other at right angles in its field of view, one can plot the position of the particle at any instant on a system of Cartesian coordinates. If the distances of these lines from each other be known, the position of the particle at the end of equal time intervals (*e.g.*, every 30 sec.) can be plotted, and hence the distance it has moved in these time intervals may be determined. Thus the average distance $\overline{\Delta}$ moved through in a given time τ can then be found. This distance depends on the forces acting on the particle, the viscous drag of the liquid, the size of the particle, and other constant factors. If the variation of $\overline{\Delta}$ with η, V, etc. predicted by theory, and the values of the constants computed from observed values of $\frac{\overline{\Delta}}{\tau}$ for a given particle, agree with values obtained in other ways, the underlying assumptions can be taken as completely verified.

The theory for this effect was first deduced by von Smoluchowski and Einstein independently about 1905, and the deduction here given is a simplified treatment due to Langevin.[8] For simplicity, it will be convenient to use not the average displacement of the particle $\overline{\Delta}$ for any time interval τ, but only the x component of

this along one of the observing axes arbitrarily chosen as the x-axis.

Assume that the particle encounters an unbalanced force X along the x-axis. It is retarded in its motion by the viscous drag which for a spherical particle is given by the constant factor in the Stokes' law equation mentioned before. This is

$$f = -6\pi\eta a v = -Kv = -K\frac{dx}{dt},$$

where v is the velocity, a the radius, and η the coefficient of viscosity. The equation of motion is, then,

$$m\frac{d^2x}{dt^2} = -K\frac{dx}{dt} + X.$$

Now x may be positive or negative along the axis, for the particle will move in one sense or the other. To get rid of the + and − signs in the equation which occur because the particle moves one way or the other; that is, to enable one to deal with the magnitude of the displacement only, it is easier to modify the equation so as to get rid of x terms and deal only with terms in x^2. To do this, one multiplies by x

$$mx\frac{d^2x}{dt^2} = -Kx\frac{dx}{dt} + Xx.$$

Now

$$x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2(x^2)}{dt^2} - \left(\frac{dx}{dt}\right)^2$$

and

$$x\frac{dx}{dt} = \frac{1}{2}\frac{d(x^2)}{dt}.$$

Hence,

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = \frac{-K}{2}\frac{d(x^2)}{dt} + Xx.$$

For a large number of displacements the xX term will, in general, cancel out, for the sign of the xX is as often positive as negative, that is, the average motion is as much in one sense as another. Thus $\overline{Xx}$, the average Xx, is zero. Also, approximately, $pV_A = R_AT = \frac{1}{3}N_Amc^2$, where V_A is the volume of a gram-molecule, R_A is the gas constant for this mass of gas, and N_A is the number of molecules in this volume. Hence the kinetic energy is $\frac{mC^2}{2} = \frac{3}{2}\frac{R_AT}{N_A}$. In dealing with the kinetic energy along the x-axis only,

the kinetic energy along x is $\frac{1}{3}$ the total kinetic energy (see Chap. IX); that is, $\frac{1}{3}\left(\frac{3}{2}\frac{R_AT}{N_A}\right)$ or $\frac{1}{2}\frac{R_AT}{N_A}$. Accordingly, one may set $\frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}\frac{R_AT}{N_A}$. The equation for the displacement as deduced above then loses the Xx term and becomes

$$\frac{m}{2}\frac{d^2\bar{x}^2}{dt^2} - \frac{R_AT}{N_A} = -\frac{K}{2}\frac{d\bar{x}^2}{dt} + 0.$$

Call

$$\frac{d\bar{x}^2}{dt} = z$$

and the result is:

$$\frac{m}{2}\frac{dz}{dt} = \frac{R_AT}{N_A} - \frac{K}{2}z,$$

or

$$\frac{dz}{z - \frac{2R_AT}{N_AK}} = \frac{-K}{m}dt.$$

Integrating this for z from 0 to z, and for t from 0 to t the result obtained is:

$$\left[\log\left(-\frac{2R_AT}{N_AK} + z\right)\right]_0^z = \left(-\frac{K}{m}t\right)_0^t,$$

$$\log\left(-\frac{2R_AT}{N_AK} + z\right) - \log\left(-\frac{2R_AT}{N_AK}\right) = -\frac{K}{m}t$$

$$z - \frac{2R_AT}{N_AK} = -\frac{2R_AT}{N_AK}e^{-\frac{K}{m}t}$$

$$z = \frac{2R_AT}{N_AK}\left(1 - e^{-\frac{K}{m}t}\right).$$

Now for finite intervals of t of the order of 10^{-5} or 10^{-6} sec. the $e^{-\frac{K}{m}t}$ vanishes. For $K = 6\pi\eta a$ and $m = \frac{4}{3}\pi a^3$, where a is about 10^{-4} cm and η is 0.01 the exponential has the value $e^{-4.5\times10^6 t}$. If t is greater than 10^{-4}, the quantity $e^{-4.5\times10^6 t}$ is negligible. Thus restricting the value of t to finite intervals τ of the order of 10^{-4} sec. or more, the quantity $d\bar{x}^2$ must be replaced by $\Delta\bar{x}^2$ and the dt by a finite interval τ in $z = \frac{d\bar{x}^2}{dt}$ and the $e^{-\frac{K}{m}t}$ vanishes. Therefore

$$\frac{\Delta\bar{x}^2}{\tau} = \frac{2R_AT}{N_AK}.$$

Accordingly,

$$\Delta\bar{x}^2 = \frac{2R_AT}{N_A}\frac{\tau}{6\pi\eta a}.$$

Thus $\Delta\bar{x}^2$, the average squared displacement of a particle due to Brownian movements along the x-axis in a time τ, is given by an equation containing the absolute temperature, the gas constant R_A, the Avogadro number, the coefficient of viscosity, and the radius of the particle. It is, consequently, open to simple experimental verification, since all these quantities may be measured, or it can be verified by seeing if $\Delta\bar{x}^2$ varies as predicted, and if N_A fits values from other data. Finally, a verification of the random

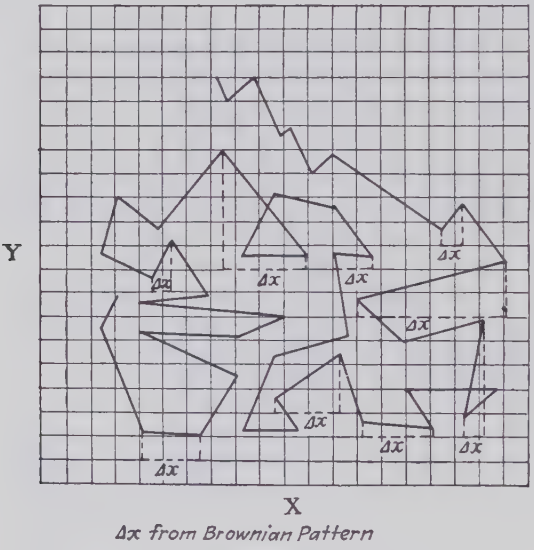

FIG. 54.

nature of the Brownian movements and the verification of the predicted law of diffusion of particles under Brownian movements deduced by Einstein give additional proof.

Perrin made these measurements using the camera lucida and a coordinate system where 16 divisions represented 5.0×10^{-3} cm. The time interval chosen was 30 sec. The average squared x component of these displacements (see Fig. 54) gives $\Delta\bar{x}^2$, and this leads to a test of the theory.

1. *Proof of the Random Nature of the Brownian Motions.*— The distribution of the x projections for a given time was found to be according to the Gauss-Laplacian law of probability which

would be expected as a result of molecular motions obeying Maxwell's distribution law, that is, out of N projections considered, $N\int_{x_1}^{x_2} \frac{1}{\sqrt{2\pi}}\frac{1}{\bar{x}}e^{-\frac{x^2}{\bar{x}^2}}dx$ should have projections lying between x_1 and x_2, the mean square $\bar{x}^2$ being measured as above. Using an emulsion of gamboge with $a = 0.211 \times 10^{-4}$ cm, the number N of displacements lying between successive multiples of the length $x_2 - x_1 = 1.7 \times 10^{-4}$ cm were as follows:

x_1 x_2	One series		Another series	
	N obs.	N calc.	N obs.	N calc.
0 and 1.7	38	48	48	44
1.7 and 3.4	44	43	38	40
3.4 and 5.1	33	40	36	35
5.1 and 6.8	33	30	29	28
6.8 and 8.5	35	23	16	21
8.5 and 10.2	11	16	15	15
10.2 and 11.9	14	11	8	10
11.9 and 13.6	6	6	7	5
13.6 and 15.3	5	4	4	4
15.3 and 17.0	2	2	4	2

This analysis and a series of others on the same subject but using different methods of representation established the completely random nature of the displacements on a quantitative basis.

2. $\overline{\Delta x}^2$ should be proportional to τ. Perrin found that, making τ 120 sec., $\overline{\Delta x}^2$ was about four times what it was for 30 sec., that is, that

$$\frac{\overline{\Delta x_{30}}^2}{\overline{\Delta x_{120}}^2} = \frac{30}{120} = \frac{1}{4}.$$

3. *The Test of the Brownian-movement Equation.*—Up to 1908, tests of the Einstein-von Smoluchowski conclusions were made using the meager data available. They yielded better than an agreement in order of magnitude.

A. The Variation with Temperature.—From the theory above, the average displacements $\sqrt{\overline{\Delta x_1}^2}$ and $\sqrt{\overline{\Delta x_2}^2}$ at two temperatures T_1 and T_2 at which the viscosities are η_1 and η_2 should be in the ratio

$$\sqrt{\frac{\overline{\Delta x_1}^2}{\overline{\Delta x_2}^2}} = \sqrt{\frac{T_1\eta_2}{T_2\eta_1}}.$$

For a temperature interval from 17 to 90°C. in one suspension, the variation should have been 2.05 for $\sqrt{\frac{\overline{\Delta x_2}^2}{\overline{\Delta x_1}^2}}$. The observed value was 2.2, which lay within the limits of experimental error for these results.

B. The Variation with η and a, and the Evaluation of N_A.—If the theory is correct, N_A should be given by $N_A = \frac{R_A T}{\overline{\Delta x}^2} \frac{\tau}{3\pi\eta a}$. If a is measured as in the law of atmospheres, then N_A will be determined. The summary of a series of results is given in the accompanying table:

100η	Emulsion	Radius $\times 10^4$ cm	Mass $\times 10^{15}$	Number of displacements	$\frac{N_A}{10^{23}}$
1	Gamboge.....	0.5	600	100	8.0
1	Gamboge.....	0.212	48	900	6.95
4–5	Gamboge in 35 per cent sugar solution.....	0.212	48	400	5.5
1	Mastic.....	0.52	650	1,000	7.25
1.2	Large mastic in 27 per cent urea solution.....	5.5	750,000	100	7.8
125	Gamboge in glycerine with 10 per cent water	0.385	290	100	6.4
1	Gamboge of very uniform quality.....	0.367	246	1,500	6.88

Thus masses varying in the ratio of 1 to 15,000 and viscosities varying from 1 to 125 gave sensibly the same value for N_A within the limits of experimental error, so that the equation is verified as regards variation of $\overline{\Delta x}^2$ with these factors. The value of N_A from the last measurements, namely, 6.88×10^{23}, lies within 1 per cent of the value found from the law of atmospheres for the best case, and is near the value 6.2×10^{23} found from L and Van der Waals' b. He therefore adopted the value 6.85×10^{23} as the true N_A. Rutherford, from measurements of the charge for α particles in about 1908, found N_A from e and the Faraday constant to be 6.22×10^{23}, and Millikan's accepted value, based on a measurement of e and a knowledge of $N_A e$, gives $N_A = 6.06 \times 10^{23}$. The proof of the nature of the Brownian movements of Perrin seems, therefore, to be quite conclusive and it may safely

be assumed that these experiments establish the validity of the kinetic theory.

4. *The Application of the Einstein Theory of Rotational Brownian Movements.*—Applying the analysis of Einstein[6] for the rotational movement of Brownian particles, which involves the assumption of the law of equipartition, Perrin was again able to obtain a value of $N_A = 6.5 \times 10^{23}$ which is in good agreement with his translational experiments. This verification therefore also establishes the validity of the equipartition hypothesis as applied to the distribution of rotational and translational kinetic energy.

5. *The Study of the Diffusion Rate of the Brownian Particles and Another Determination of N_A.*—A still further value of N_A was obtained from the diffusion rate of mastic particles in glycerine solutions by Brillouin[9] under Perrin's direction. Einstein predicted that the coefficient of diffusion D should be given by the relation

$$D = \frac{R_A T}{N_A} \frac{1}{6\pi\eta a}$$

for solutions where the particles were so large that the Stokes law relation held. By measuring D in an ingenious manner, Brillouin was able to evaluate N_A, and found it to be 6.9×10^{23}; in agreement with the earlier work of Perrin on displacements. The absolute values of Perrin for N_A, while consistent with themselves, are, as a whole, higher than those from Van der Waals' b, and from Rutherford or Millikan's values. This difference does not lie in any fault of the theory. It lies chiefly in the inaccuracies present in the difficult measurements of Perrin, notably on the value of a. Another error of some significance in these results lies in the assumptions of Stokes' law as Millikan[3] has shown. As the error was the same throughout, it makes the results of Perrin consistent. Where it was eliminated Millikan was able to get an accurate verification.

89. Accurate Verification of the Brownian-movement Relations for Gases, and the Determination of the Avogadro Number. *A. Verification of the Brownian-movement Relations for Gases.*—In all Perrin's work the accuracy of the results was limited by the difficulty of evaluating a, the radius of the particles, and also in the Brownian displacement measurements by the uncertainty of the validity of Stokes' law assumed for the small particles used. Furthermore, the results are based on analogy between colloidal suspensions and particles in a gas acted on by molecular impacts.

They are thus open to some theoretical criticism as a complete proof. Millikan overcame this objection in a very striking manner. He worked with minute droplets of oil floating in air or H_2. These took on a spherical form, owing to cohesive forces. He eliminated at one stroke both the assumption of correctness of Stokes' law and the uncertainty in the determination of a by a technique used in the determination of the elementary charge e. To accomplish this, he charged the drop electrically and studied first the lateral Brownian displacements of the drop when suspended in the air, then its rate of fall under gravity alone, and finally under gravity which was opposed by an electrical field acting on the charged drop. The measurements were carried out by Millikan and Fletcher[33] in 1911. As was shown in Sec. 88, a particle undergoing Brownian movement is assumed to be retarded by a viscous force $F = -Kv$. If the Stokes' law holds, $K = 6\pi\eta a$. If it is possible that it does not hold, the use of an undetermined factor K is more accurate for the discussion. Now it is this constant K which depends on a, and, as the law may not hold, the indeterminate form will be used. Assume the particle for which the Einstein equation holds in the form

$$\overline{\Delta x^2} = \frac{2R_A T}{N_A}\frac{\tau}{K},$$

to be placed in a uniform electrical field of strength F parallel to the earth's field. Assume that it has an electrical charge $e\nu$ on it (where e is the electron and ν is some whole number), of such a sign that the force acting on the particle opposes the action of gravity. The drop will then fall under the force mg of gravity with a velocity v_1 if the field is absent. If the field F acts on the drop, it will fall with a retarded speed v_2 under the force $mg - Fe\nu$. Since the retarding force is the same in both cases and the fall is uniform, then

$$\frac{v_1}{v_2} = \frac{mg}{Fe\nu - mg} \quad \text{or} \quad \frac{Fe\nu}{mg} = \frac{v_2 + v_1}{v_1}$$

$$\nu e = \frac{mg}{Fv_1}(v_2 + v_1).$$

Now Stokes' law says that $mg = Kv_1$, so that $\frac{mg}{v_1} = K$. Therefore $\nu e = \frac{K}{F}(v_2 + v_1)$. For ν equal to unity, $e = \frac{K}{F}(v_2 + v_1)_0$ and $K = \frac{eF}{(v_1 + v_2)_0}$.

Now Millikan in a separate series had actually determined e, so that it was easy to get ν and to find the value for $\nu = 1$. Actually, e need not have been known, for $e = \frac{K}{F}(v_2 + v_1)_0$ could be found by charging the drop a number of times to different values, and finding the least common divisor for $\frac{K}{F}(v_2 + v_1)$. This would give $\frac{K}{F}(v_1 + v_2)_0$. Thus one could obtain K by observation from v_1, v_2 and F and e.

Putting the value for K into the Brownian-movement equation above, then at once

$$\overline{\Delta x}^2 = \frac{2R_AT}{F}\frac{(v_1 + v_2)_0}{N_Ae}\tau$$

or

$$N_Ae = \frac{2R_AT}{F}\frac{(v_1 + v_2)_0}{\overline{\Delta x}^2}\tau.$$

If, accordingly, the Brownian-movement theory is correct, measurements of $\overline{\Delta x}^2$ and $(v_1 + v_2)_0$ for a given τ, T, and F should yield N_Ae, the Faraday constant for the electrolysis of a univalent ion. In these experiments Millikan and Fletcher first held a drop suspended between the plates and measured its Brownian motion along a line normal to the direction of sight and gravity, timing the transits of the drop across cross-hairs of known distance in the eyepiece of the telescope. By using gases of low η and working at lower pressures, values of $\overline{\Delta x}^2$ could be worked with 50 times as large as those of Perrin for the same drop. Hence much more accurate measurements were possible. Next the drop was allowed to fall in the absence of F, and v_1 was determined. Then it was charged to varying amounts and v_2 was measured. From these measurements $(v_1 + v_2)_0$ was determined for a given F. The measurements as made gave the average Δx for a given τ. For convenience, $\overline{\Delta x}$, the average, was computed and then squared. This gave $(\overline{\Delta x})^2$. In the Brownian-movement equation the average of the squares $\overline{\Delta x}^2$ occurs. Thus, to insert the values for Δx observed into the equation above, it is necessary to employ the relation $\overline{\Delta x} = \sqrt{\frac{2}{\pi}\overline{\Delta x}^2}$, whence $N_Ae = \frac{4}{\pi}\frac{R_AT}{F}\frac{(v_1 + v_2)_0}{(\overline{\Delta x})^2}\tau$.

The temperature in these measurements was also easily more accurately controlled by a thermostat than in those of Perrin. The results should, consequently, be more reliable. With 1,735 displacements on a drop with unit charge, Millikan and Fletcher got $N_A e = 2.88 \times 10^{14}$ electrostatic units (e.s.u.). For a univalent ion in electrolysis, $N_A e$ comes out as 2.89×10^{14} e.s.u. The probable error on the number of counts used is 2 per cent and the observed difference is well within this limit. Both in the accuracy of the result and in the avoidance of any questionable assumptions this beautiful piece of work confirms Perrin's conclusions in a striking manner and can be regarded as one of the triumphs of modern technique in experimental kinetic theory. It definitely establishes the correctness of the kinetic-theory explanation of Brownian movements and thus verifies the kinetic theory of matter beyond a doubt.

B. Determination of the Avogadro Number.—As indicated in Sec. 85, by 1908 there were but one or two values of the number of molecules per cm^3 (Loschmidt's number) or the number of molecules in a gram-molecule (Avogadro's number), and these were uncertain in the tens of per cent. With the work of Perrin and the development of precision in the newer fields of radioactivity and atomic structure, 1913 already saw several independent and accurate evaluations of this important constant. In 1926, when the first edition of this book was in the process of being written, already some seven or more methods giving sensibly the same value of this number were well developed. In the intervening seven years, the number of methods has jumped to more nearly a score. In fact there are so many ways in which this number can be estimated that it is difficult to determine the exact number, owing to the interrelations of the quantities used in different methods. In a recent article, Virgo[32] summarizes the measurement of this quantity. In it he states that more than 80 different experimental evaluations have been made to date. In this section it appears desirable to depart from Virgo's excellent analysis and proceed according to a different scheme. For the purpose of discussion, methods will be termed *independent* if by these different methods a quantity is evaluated which in combination with other relations previously used yields the value of the number. For example, as will be seen, the Faraday constant Ne can be used to yield N by combining it with the

value of e yielded by any one of the many methods giving e, and any such method can fairly be called an independent method.

In detailing these methods, a number of them may be grouped under a common heading. These are as follows:

1. The combination of the Faraday constant with the value of the electron e determined in three different ways, to wit:

a. Millikan's oil-drop measurement.

b. Rutherford's measurement of the charge on the α particle and the knowledge that the particle is a doubly charged He atom.

c. From the average fluctuations in thermionic emission for a given current with known capacity and resistance in the circuit, e is evaluated.

2. Radioactive measurements yield the value of N directly in two ways. If the number of α particles (doubly charged He atoms) emitted per gram of Ra per second can be evaluated accurately by scintillation counts or Geiger counter, the value of N can be determined by:

a. The measurement of the volume of He gas produced per year per gram of Ra.

b. The measurement of the decay constant of Ra or of Io (if the number of α articles emitted per second from this are known).

3. Kinetic-theory methods yield a number of ways of evaluating N_A. These fall under several heads:

a. Mean free path:

(1) Evaluation of the mean free path from the coefficient of viscosity. Combined with the evaluation of another relation between molecular radius and the number of atoms in unit volume by measurement of:

(2) Van der Waals' b from either the Joule-Thomson effect or critical data.

(3) The molal volume of the substance in the liquid state.

b. Evaluation of Boltzmann's constant k defined by $k = R_A/N_A$. Hence as R_A is known, N_A can be evaluated. This can be accomplished by the following means:

(1) From the average Brownian displacement of a small mass on a pendulum of known period and moment of inertia.

(2) From the fluctuations of potential across a resistance produced by the thermal agitation of the electrons.

c. From the law of atmospheres for colloidal suspensions.

d. From the study of the Brownian displacements of particles in a solution or suspended in a gas, or by the rate of diffusion of such particles in a solution or gas.

e. From the change of viscosity of a solution on dilution by the solute.

f. From the adsorption of molecules on liquid surfaces.

g. From fluctuations of density, critical opalescence, and miscibility.

4. From X-rays by measuring the wave length with a ruled grating at grazing incidence and applying this to determine the spacing of crystal planes in a crystal of known structure, one obtains, by means of the density of the crystal, an accurate value of the Avogadro number.

5. From the molecular scattering of light by molecules, notably the sky, Rayleigh showed that the value of the Avogadro constant could be determined.

6. By the intercombinations of many equations resulting from modern investigations of spectral and atomic structural nature which contain two or more of the fundamental physical quantities such as the Planck constant h, the electron e, the mass m of the the electron, and the Boltzmann constant k. There are some eleven relations of this nature which can be intercombined effectively to give either e, or k and hence N_A. It is futile to attempt to determine the number of different independent combinations which can be used. It suffices, however, to give the phenomena involved in order to illustrate the diverse ways in which this important constant appears:

a. From the photoelectric-effect and ionization-potential studies with either light or X-rays, one has h/e.

b. From the atomic-diffraction experiments of Stern and Estermann, one evaluates h/m, when m is the mass of the atom diffracted.

c. From the Stern-Gerlach determination of the magnetic moments of atoms and the evaluation of the Bohr magneton, one obtains $\frac{e}{m}h$.

d. From three different procedures one can evaluate e/m for electrons; these are:

(1) Electric- and magnetic-deflection experiments on electrons.

(2) From the simple Zeeman effect on certain types of spectroscopic lines.

(3) From the Rydberg constant for He^+ and H atoms.

e. From the fine-structure constant α which can be derived from certain spectra, one evaluates e^2/h.

f. From the Rydberg constant for infinite mass, R_∞, one evaluates $\frac{e}{m} = \frac{2\pi^2 e^5}{h^3 c^2 R_\infty}$.

g. From the Wien displacement law $\lambda_{max} T = c_2/\beta$, one can evaluate h/k.

h. From the Planck radiation law and the Stefan-Boltzmann constant, one evaluates h^3/k^4.

i. From the Compton shift in X-ray wave lengths, one obtains h/m.

j. From electron-diffraction experiments, one obtains the de Broglie wave length λ which gives h/m if the velocity v of the electron is known.

Owing to lack of space it is impossible to discuss the methods in detail. In most cases the equations will be given together with the references and comments as to the accuracy of the method. In this discussion it will be assumed that as $N_A e$, the Faraday, and $R_A = N_A k$, the gas constant per mole, are known, N_A is at once found if e or k is evaluated.

1*a*. The evaluation of e by the oil-drop method of Millikan[3] is believed by Birge[10] to give the most accurate value of e and hence of N_A. The method is indicated in the first part of this section and is given in detail in Millikan's book "The Electron." It is too well known to be repeated here. The value of $N_A = 6.064 \pm 0.006 \times 10^{23}$ and $e = 4.77 \times 10^{-10}$ e.s.u.

1*b*. Rutherford[11] and Geiger caught the α particles from a fixed quantity of radium over a given solid angle in a Faraday cage for a given time and measured their charge. The number of α particles from the same radium emitted over a smaller solid angle was determined by the scintillation method. As the α particle carries two units of positive charge as shown by e/m measurements, it is simple to obtain the charge on the α particle and hence e. The value found by Rutherford was 4.65×10^{-10} e.s.u. and by Regener was 4.76×10^{-10} e.s.u. The method was one of the first accurate determinations of e. Its weakness lies in the difficulty of catching all the α particles without loss of charge or secondary effects and in the uncertainty of scintillation counts. The modern Geiger counters are now much more reliable and the method can be improved.

1*c*. Schottky[12] showed that for weak thermionic currents the fluctuations of the current were due to the irregular liberation of electrons by the hot filament. Since this is a purely statistical phenomenon, it is amenable to statistical treatment. Analysis shows that the alternating current excited in a tuned circuit by the fluctuations in thermionic emission has a mean square value given by $\bar{J}^2 = i_0 e/2RC$, where i_0 is the thermionic current, R is the resistance, and C the capacity of the tuned circuit. Hull and Williams in this fashion determined the mean value of e as 4.76×10^{-10} with a variation lying within 2 per cent of the mean value.

2*a*. Dewar,[13] and later Boltwood and Rutherford, determined the volume of He produced by radium. The value obtained was 163 mm^3 per year per gram of Ra element. This combined with the number of α particles given out per gram of Ra element per year gives the number of He atoms in 163 mm^3 of He, for each α particle gives 1 He atom when neutralized. The method is inaccurate because of the difficulty of measuring small quantities of He, the loss of He by occlusion in the walls, and the uncertainty in the exact value of the number of α particles per gram of Ra per second (now given as 3.7×10^{10}). The method is, however, a very direct method and gives a value in accord with those from other methods within the accuracy of the method. The value of N_A was 6.0×10^{23} for Dewar and 6.6×10^{23} for Boltwood.

A modification of this method arises from the fact that each α particle emitted from a given amount of radium per second represents the production of an atom of radon. If λ is the decay constant of radon, then if Q α particles are emitted from a gram of radium per second, the condition for equilibrium between production and decay of radon yields the number of atoms of radon present at any time as $n = Q/\lambda$. Now $n = NV$, where N is the Loschmidt number and V is the volume of radon in equilibrium. Thus $N = Q/\lambda V$ and as Q and λ are known, if V can be measured, N can be evaluated. Wertenstein[32] measured V as 6.39×10^{-4} cm^3 for 1 curie of radium and obtained a value of N_A of 6.16×10^{23}.

2*b*. Radioactive substances decay according to the law $n = n_0 e^{-\lambda t}$, where n is the number of atoms present at t, n_0 is the number present at $t = 0$, and λ is the radioactive-decay constant which can be measured. Knowing Q_0, the number of

α particles emitted per gram of Ra per second, one can calculate the number of α particles emitted during the course of the lifetime of 1 gram of Ra. Since each atom of Ra emits one α particle, one can write

$$Q = \int_0^\infty Q_0 e^{-\lambda t} dt = \frac{Q_0}{\lambda},$$

whence the number of atoms in a gram of radium is known once λ is known, and multiplication by the atomic weight gives N_A.[14] This method suffers from the inaccuracy both in Q_0 and in the evaluation of λ. It is, however, noteworthy in that it is a direct evaluation. The method has been used by Boltwood, Meyer, and Schweidler, Keetman, and Ellen Gleditsch[32] and gave values between 7.6 and 6.35 $\times 10^{23}$ for N_A.

3*a*. The mean free path of a gas molecule as defined by Tait is given by $L_T = 1.05/(\sqrt{2}\pi\sigma^2 N)$ (see Sec. 39). The mean free path can be evaluated in different ways, the most accurate values being yielded by the coefficient of viscosity $\eta = 0.499\rho\bar{c}L$. Since $C = \sqrt{3p/\rho}$ and $\bar{c} = \sqrt{8/3\pi}C$, it is clear that η will give a value of L. It is also clear that L depends on the value of σ and the Loschmidt number N. Hence any independent measurement of a quantity depending on N and σ alone will give either one. From critical data Van der Waals' constant $b = 2/3\pi\sigma^3 N$ can be evaluated. This, combined with the mean free path, will give N. The value of b can also be obtained from the isotherms and from the Joule-Thomson effect. The molal volume of a substance in the liquid state enables one to obtain another expression involving σ and N. This gives $V = (2/3\pi\sigma^3 N)a$, where a is a coefficient less than unity expressing the packing coefficient. All these methods suffer from a serious defect as regards accuracy, in that the constants in expressions for L, η, a, etc., cannot be accurately known, owing to mathematical complexity. Furthermore, the quantities σ and also L determined by different methods are not the same, since their definition is imposed by the condition of measurement. It is thus clear that, while such methods can give an approximate value of N_A, the agreement to be expected with more accurate determinations is no better than the theoretical and experimental uncertainty which may exceed 10 and 20 per cent.

3*b*. The kinetic theory, by means of heat conditioned fluctuations, enables the Boltzmann constant k to be evaluated:

(1) E. Kappler[15] studied the fluctuations in displacement of a small vertical mirror suspended from a small quartz fiber as a result of the unequal bombardment due to molecular impact. The average squared angular displacement $\overline{\phi^2}$ is related to the directed force D (due to torsion) by the relation $D\overline{\phi^2} = kT$, where T is the absolute temperature. To evaluate D, one uses the relation that the period of oscillation $T^2 = 4\pi^2\frac{I}{D}$, where I is the moment of inertia and D is the force constant. I can be evaluated by loading the system with a small mass of known moment of inertia and measuring the altered period T'. The gas pressure was varied from atmospheric pressure to 10^{-4} mm of Hg. This very delicate but direct method was carried out and after 101 hr. observation yielded a value of k which gave N_A as $6.059 \times 10^{23} \pm 0.6$ per cent, an excellent value.

(2) J. B. Johnson[16] showed that the so-called tube noise in vacuum-tube amplifiers is due to fluctuations of potential between the terminals of a conductor. This fluctuation is due to the thermal agitation which causes a small but definite mass motion of the electrons giving rise to potential differences. From the assumed random nature of these fluctuations, Johnson showed that the observed average square fluctuation of the current $\overline{I^2}$ is given by

$$\overline{I^2} = \left(\frac{2kT}{\pi}\right)\int_0^\infty R(\omega)\left|Y(\omega)\right|^2 d\omega,$$

where k is the Boltzmann constant, T is the absolute temperature, $R(\omega)$ is the real component of the impedance of the conductor, $Y(\omega)$ is the transfer impedance of the amplifier, and $\omega/2\pi$ is the frequency. From measurements Johnson obtained $k = 1.27 \times 10^{-16}$ erg per degree with a mean deviation of 13 per cent. This gives N_A as 6.54×10^{23} which is about 8.5 per cent higher than the accepted value.

3*c*. The evaluation of N_A by Perrin[2] from the law of atmospheres has been adequately discussed in Sec. 87. Later measurements are due to Westgren,[17] Svedberg,[17] and Shaxby.[17]

3*d*. The Brownian-movement studies of Perrin have been discussed *in extenso* in Sec. 88 and no more need be said. The chief drawback to this and the preceding methods lies in the impossibility of an accurate evaluation of drop or particle size

and mass. Later applications of this method are due to Westgren, Svedberg, Nordlund, and Shaxby.[17] Fletcher[33] applied the method to Hg droplets in air and Schmid[33] to selenium particles. Fletcher found $N_A = 6.03 \pm 0.03 \times 10^{23}$. Similar results to these for solutions have been obtained for the coefficient of diffusion $D = \frac{RT}{N_A}\frac{1}{6\pi\eta a}$ in contrast to $\overline{\Delta x}^2 = \frac{RT}{N_A}\frac{1}{3\pi\eta a}$, where D is the coefficient of diffusion of the particles. Here again a must be estimated to obtain N_A from measurements on D.

3*e*. Einstein,[18] on the assumption that large molecules such as sugar diffusing in a solution behave like spheres in a homogeneous medium, deduced a relation for the viscosity of a solution which states that the ratio of η_s, the viscosity of the solution, to η, that of the pure solvent, is given by the relation

$$\frac{\eta_s}{\eta} = 1 + 2.5n\left(\frac{4}{3}\pi a^3\right)$$

Here a is the hydrodynamic radius of the assumed spherical sugar molecule, and n is the number of sugar molecules per cm^3 of solution. The diffusion coefficient of these same spherical molecules is given by

$$D = \frac{RT}{N_A}\frac{1}{6\pi\eta a}.$$

Since $n/N_A = m/M$, where m is the mass per unit volume and M is the molecular weight, we have $n = N_A\frac{m}{M}$ whence $\frac{\eta_s}{\eta} = 1 + 2.5\pi\left(\frac{4}{3}\right)N_A\frac{m}{M}a^3$ which, combined with the expression for D, gives N_A. This equation, while accurate in order of magnitude, like all kinetic-theory equations, is uncertain in the magnitude of the constants so that it is not of great value.

3*f*. Lecomte du Noüy[32,37] studied the adsorption of organic molecules on a liquid surface in monomolecular layers using methods initiated by Langmuir. He measured the adsorption of sodium oleate on water. There appeared to be three critical areas for surface distribution of these layers. These three areas were interpreted by du Noüy as representing layers in which the molecules were arranged with one each of their three axes (assumed at right angles) perpendicular to the surface. Thus, from the density of the molecules in the three layers, assuming

them to be monomolecular, du Noüy calculated the extension of the molecules along the three axes. From these three dimensions for these molecules he obtained the volume of the molecules by multiplying the figures together. From the density of the substance and the molecular weight the Avogadro number was calculated as $N_A = 6.003 \times 10^{23}$. While the agreement is fortuitously good and the interpretation seems reasonable, there is considerable doubt as to the validity of the reasoning and hence as to this method. Alexander points out the uncertainty of the method quite clearly.

3*g*. Aside from the methods outlined above, the fluctuations in density, which is a molecular phenomenon, a study of the critical opalescence, and studies on the miscibility of two liquids have led to very rough evaluations of N_A in the hands of Constantin,[32] Keesom and Onnes,[32] and Fürth[32] and Zernike.[32] The values range from 6×10^{23} to 7.7×10^{23}.

4. In recent years the measurement of absolute X-ray wave lengths by diffraction at grazing incidence by ruled gratings has been developed to a high degree of precision.[19] Hence X-ray wave lengths are certainly and accurately known. If such X-rays are scattered from a crystal of known structure, the crystal X-ray spectrum relates the wave length λ to the grating space by the equation $\lambda = 2d \sin \theta$. Thus if corrected for the index of refraction of the crystal, the true grating space d' of the crystal can be found to a considerable degree of precision. This quantity d' is given by $d' = \{nM/[\rho N \phi(\beta)]\}^{1/3}$, where $n = 1/2$, M is the molecular weight of calcite, ρ is the density, and $\phi(\beta)$ is a geometrical constant depending on the crystal structure of calcite. If the crystal structure is regular, the accuracy claimed for the method approaches, if not exceeds, that of the oil-drop method in evaluating e. The value of e obtained from this value of N is definitely higher than Millikan's value, *i.e.*, of the order of $e = (4.794 \pm 0.024) \times 10^{-10}$ e.s.u. It is today an open question as to which result is the most accurate, as some doubt is being cast on Millikan's value on account of the uncertainty of the coefficient of viscosity of air used in its calculation.

5. The explanation of the blue color of the sky in terms of molecular scattering was originally due to Lord Rayleigh. In the theory it appears that the intensity of the scattering depends on the number of molecules per unit volume involved in the

scattering. Modern techniques made it possible for Dember[20,34] to evaluate the Loschmidt number N from the intensity of the light E_1 and E_2 scattered at angles of ϕ_1 and ϕ_2 with the sun using a photoelectric cell. Operating from Monte Rosa and the Peak of Teneriffe, where the air was free from dust, $N = N_A/22{,}410$ was evaluated by

$$N = \frac{32\pi^3}{3}\left\{(\mu - 1)^2 M H_0 \frac{T}{273}\frac{1}{\lambda^4}\frac{b}{b_0}\frac{\csc\phi_1 - \csc\phi_2}{\log E_2 - \log E_1}\right\}.$$

Here μ is the index of refraction, M the modulus of the natural system of logarithms, H_0 the height of the homogeneous atmosphere, b_0 the barometric pressure at sea level, b the pressure at the point of observation, λ the wave length of the light used, and T the absolute temperature. Dember obtained a value of $N_A = 6.48 \times 10^{23}$. The method is in itself sound, but the measurements are subject to serious errors due to the inability to control natural disturbances such as dust and due to the variable density of the air from which the light is scattered. Fowle,[34] by an indirect but ingenious and more accurate method, using this principle found N_A to be $(6.06 \pm 0.04) \times 10^{23}$.

6. As stated in the summary there are a large number of equations derived by experiment from atomic or electronic structures and behavior which give relations between e the electron, h the Planck constant of quantum action, m the electronic mass, and Boltzmann's k, and thus, by solution for k or e, yield the value of the Avogadro number. The combinations which can be used to give this constant are very many and will not be indicated, as but few of them are of great enough accuracy when combined to be of importance. They present, however, new independent ways of evaluating N_A and thus help to confirm the belief in this fundamental concept of kinetic theory which was denied by the school of energetics.

6*a*. In the photoelectric effect, the Einstein[21] equation says that $\frac{1}{2}mv^2$, the kinetic energy of an electron liberated by ultraviolet light or X-rays from a metal surface, is given by $\frac{1}{2}mv^2 = Ve = h\nu - h\nu_0$. Here m is the mass of the electron, v is its velocity, V is the potential through which an electron of charge e must fall to get the energy $\frac{1}{2}mv^2$ (*i.e.*, the opposing potential required just to annihilate the velocity v of the electron), h is the Planck constant, and ν is the frequency. $h\nu_0$ is the photoelectric threshold, *i.e.*, the energy required just to liberate an

electron from the surface against the electrical forces which hold it. Thus ν_0 is the limiting frequency to just cause a photoelectric effect. ν_0 can be measured as the photoelectric threshold or from the work function of the metal obtained from thermionics, and V can be measured as can ν. Thus one could obtain a value for h/e. It is easier to eliminate $h\nu_0$ by changing ν and observing the stopping potential V. From the slope of the curve $dV/d\nu = h/e$, this ratio can be accurately evaluated.

From. the ionizing potential of an atom, *i.e.*, the energy expressed as volts free fall of potential required to give the electron a velocity sufficient to remove an electron from another atom of known sort, one can determine the ratio h/e. The same could be done for the potential required to excite an atom to any given frequency of emission ν. From spectroscopic measurements, ν_e and ν_i for excitation and ionization can be determined with high precision. The potentials V_e and V_i can, however, be measured to a tenth of 1 per cent only, owing to the velocity distribution of the electrons used. Hence from the relations $h\nu_e = V_e e$ and $h\nu_i = V_i e$, one can get e/h. The values obtained from both methods are fairly accurate, but are not so good as the values from the determination of e by Millikan's method.

6*b*. Recently Estermann, Frisch, and Stern[22] have succeeded in diffracting atoms of He and molecules of H_2 from the crossed grating lattices of NaCl and LiF crystals. According to the wave mechanics, the atoms and molecules have a wave length λ given by $\lambda = h/mv$, where *m is the mass of the molecule or atom*, h is the Planck constant, and v is the velocity of the atom or molecule. Using a molecular-velocity analyzer and measuring λ from the angle of diffraction and the grating constant of the crystal, they succeeded in obtaining values of λ good to about 1 per cent. From the relation $\lambda v = h/m$, one has a relation between h and m, the mass of the atom or molecule. This can be used with values of h from other equations to give m. The Avogadro number is then found from $N_A m = M$, where M is the molecular or atomic weight in grams.

6*c*. The beautiful Stern-Gerlach experiments proving the quantization of magnetic moments and evaluating the Bohr magneton lead to another relation between e/m and h of considerable precision. The most accurate recent study is that of Meissner and Scheffers[23] who projected a beam of Li atoms or K

atoms through an inhomogeneous magnetic field at right angles to their path. This caused a separation of the beam into two parts, those of atoms with one Bohr magneton parallel and the other with one Bohr magneton antiparallel to the field. From the separation, or better, displacement, of the beam, μ, the magnetic moment of the Bohr magneton, can be determined. The relation is $\mu = \frac{2kT}{A}S_\alpha$, where kT is the kinetic energy of the molecules, S_α is the displacement of the molecules having the most probable velocity $\alpha = \sqrt{2kT/m}$, and A is given by $A = \int_0^l dl \int_0^l \frac{\partial H_z}{\partial z} dl$, l being the length of the beam in the field H, and H_z being the component of the field normal to the beam. They obtained a value for $\mu = (0.916 \pm 0.005) \times 10^{-20}$ for the Bohr magneton. The Bohr theory evaluates the magnetic moment μ for such an atom as $\mu = \frac{e}{m}\frac{h}{4\pi}$. Whence this measurement gives a relation between e/m and h. This can be combined with e/m evaluations to give h, or with the value of h/m from the electron-diffraction experiments (see 6*j*) to give e.

6*d*. The quantity e/m can be evaluated with great precision by one of three methods, the first being direct, the other two indirect from spectroscopic measurements.

(1) The earliest measurements of J. J. Thomson showing that the cathode rays were negatively electrified particles evaluated e/m and v for these particles by electrical and magnetic deflections. Today free electrons accelerated by a known field and separated out by a magnetic velocity analyzer are subjected to deflections by electrical or magnetic fields, and e/m is measured. Several devices using oscillating potential differences have also been tried to get accurate values.[24,36] The value of e/m appeared to be higher for this method than that yielded by spectroscopic methods. Recent results indicate a downward trend in value toward that obtained from spectroscopy.

(2) The simple Zeeman effect by which a spectroscopic line is broken up into three components when the source is placed in a magnetic field and is viewed transversely to the field gives e/m according to the equation $e/m = 4\pi c\Delta\lambda/\eta H\lambda^2$, where $\Delta\lambda$ is the separation of either component of a normal triplet of wave length λ, c is the velocity of light, H is the magnetic field, and

η is the index of refraction of the medium in which λ and $\Delta\lambda$ are measured. The best result, according to Birge,[10] is that of Babcock[25] which has a probable error of some 2 parts in 1,700.

(3) Sommerfeld in his "Atomic Structure and Spectral Lines," 5th German ed., Chap. II, Sec. 5, indicates the effect on the simple Bohr theory due to the motion of the nucleus as well as the electron owing to the finite mass ratio of the two. The effect is to alter the Rydberg constant given to the Bohr theory by dividing the Rydberg constant for a nucleus of infinite mass by the factor $1 + m/m_{\mathrm{H}}$, where m is the electronic mass and m_{H} is the mass of the H nucleus, which is chosen for illustration. This enables the ratio of the mass of the electron to be related to the mass of the H nucleus by means of the Rydberg constant for infinite nuclear mass and the same constant for H. An analogous expression can be derived for He in which m_{He} replaces the m_{H} above. Between these equations one eliminates the Rydberg constant for infinite mass and from the relative masses of He and H atoms one obtains a relation in terms of the masses of He and H atoms which gives the ratio $\frac{m}{m_{\mathrm{H}}}$. As $\frac{m}{m_{\mathrm{H}}} = \frac{e/m_{\mathrm{H}}}{e/m}$, one can write

$$\frac{m}{m_{\mathrm{H}}} = \frac{\frac{e}{m_{\mathrm{H}}}}{\frac{e}{m}} = \frac{(R_{\mathrm{He}} - R_{\mathrm{H}})(\mathrm{He} - m)}{R_{\mathrm{H}}(\mathrm{He} - \mathrm{H} - m)},*$$

where R_{He} and R_{H} are the observed Rydberg constants for He^+ and for H, while He, H, and m represent the atomic weights of helium, hydrogen, and electron, respectively. Now $\frac{N_A e}{N_A m_{\mathrm{H}}}$ is the Faraday constant F divided by $\mathrm{H} - m$. Hence one can write

$$\frac{e}{m} = \frac{FR_{\mathrm{H}}(\mathrm{He} - \mathrm{H} - m)}{(R_{\mathrm{He}} - R_{\mathrm{H}})(\mathrm{He} - m)(\mathrm{H} - m)}.$$

Thus e/m was accurately evaluated by Houston[26] in recent years. The value obtained is $(1.761 \pm 0.001) \times 10^7$ absolute electromagnetic units (abs. e.m.u.) per gram and has one-half the probable error of Babcock's value. It is in agreement with the

* The symbols He and H in these equations stand for the atomic weights of He and H atoms, *i.e.*, for $N_A m_{\mathrm{He}}$ and $N_A m_{\mathrm{H}}$.

latter, and both are below the earlier deflection values by about 8 parts in 1,700.

Thus the values of these ratios are available for combination with appropriate ratios from other experiments for accurate evaluation of the Avogadro number.

6*e*. Sommerfeld[27] originally successfully explained the fine structure of the spectral lines in the Balmer's series for H and in the case of He^+ by placing the relativity correction for the variation of mass with velocity into the Bohr formulation. A constant α, occurring in the complex equations resulting, called the *fine-structure constant*, is given by $\alpha = 2\pi e^2/hc$, where c is the velocity of light. The value of α, as given by Birge,[1] is $\alpha = (7.283 \pm 0.006) \times 10^{-3}$. The early evaluation of α was quite accurate but was purely fortuitous as the electron spin was neglected. It happened that the original assignment of quantum numbers by Sommerfeld was in error and this led to the agreement. With the discovery of electron spin and the proper assignment of quantum numbers, the evaluation of α is again possible and is in agreement with older values. X-rays, where electron spin does not play such a rôle, also enable the accurate evaluation of α. Hence one has another combination of e and h which can lead to a determination of e when combined with item 6*a* above.

6*f*. The Rydberg[28] constant for a nucleus of infinite mass R_∞ enables a relation between e, m, and h to be obtained. This constant R_∞ is given by

$$R_\infty = \frac{2\pi^2 e^5}{h^3 c^2 \left(\frac{e}{m}\right)}.$$

Now R_∞ can be deduced from the observed value of this constant for H by the relation

$$R_\infty = R_H\left(1 + \frac{m}{m_H}\right) = R_H\left(1 + \frac{F}{\frac{e}{m}(H - m)}\right)$$ (see part (3) of item 6*d*).

It is clear that while the values of the quantities involved are very accurate, the expression is too involved and requires combination with too many other relations to give a good value of N_A. It does, however, furnish another set of values.

6*g*. From the Wien[29] displacement law for black-body radiation $\lambda_{max.}T = c_2/\beta$, where $\beta = 4.9651$ and c_2 is the radiation constant. As $\lambda_{max.}$ and T are capable of accurate measurement, c_2 can be evaluated, and Birge gives the value of $c_2 = 1.432 \pm 0.003$ cm degree. Since Planck's black-body radiation law evaluates c_2 and $c_2 = hc/k$, one can at once evaluate h/k. This, combined with a value of h from any combination of data giving h, gives several ways of evaluating k and hence N_A.

6*h*. The Stefan-Boltzmann[30] constant for the energy radiated by an ideal black body at $T°$ abs. reads $E = \sigma T^4$. σ can be evaluated from radiation measurements and Birge gives for this $\sigma = (5.735 \pm 0.011) \times 10^{-5}$ erg cm^{-2} deg.$^{-4}$ sec.$^{-1}$ Since σ is by Planck's radiation law related to h and k by the equation $\sigma = \frac{2\pi^5 k^4}{15c^2h^3}$, one has another relation between h and k, k^4/h^3, from which one can, as in 6*g*, obtain a value of k or obtain one by combination with 6*g* itself. Other evaluations of the relation between h and k can also be obtained from the distribution-law curves themselves but will not be so accurate as the values given above, owing to the inaccuracy of the physical measurements.

6*i*. The effect discovered by A. H. Compton,[31] in which X-rays scattered from loosely bound (*i.e.*, practically free) electrons in light atoms are shifted in wave length by an amount $\Delta\lambda$ (wave length is lengthened) when they are scattered through an angle ϕ with the original direction where $\Delta\lambda$ is given by $\Delta\lambda = \frac{h}{mc}(1 - \cos\phi)$, gives another independent method of evaluating a useful ratio. Since ϕ and $\Delta\lambda$ are capable of measurement to a considerable degree of precision, it is clear that the ratio h/m can be obtained. The combination of this value with that in item 6*b* gives an independent evaluation of h or of m which can be combined with any relations desired to give e or k and hence N_A. To date the values are not so accurate as they might be.

6*j*. Relatively recently the study of electron diffraction by metal foils has experimentally been placed nearly on a par with e/m determinations in accuracy. From the study of the electron-diffraction experiments from known lattices using electrons of homogeneous and known velocities, λ the de Broglie wave length and v the electron velocity can be accurately measured. With such a method Meibom and Rupp[35] evaluated λ and v. The

de Broglie wave length λ is related to h, m, and v by the well-known equation $\lambda = h/mv$. Since, according to relativity for the fast electrons $m = m_0/\sqrt{1 - v^2/c^2}$, the relation used is $\lambda = \frac{h}{m_0 v}\sqrt{1 - \left(\frac{v}{c}\right)^2}$, where m_0 is the mass of the electron at rest. Hence, since λ and v are known, a value for the ratio of h/m_0 is obtained having some precision. The authors do not calculate h/m_0 from their results, but e/m_0 is taken from Kirchner's[36] data and the value of h/e is then determined. This ratio was found to be $h/e = (1.3798 \pm 0.0033) \times 10^{-17}$ (e in electrostatic units, h in erg $\times$ seconds). This value is distinctly higher than other values of the same ratio, which range from 1.3714 to 1.375 by perhaps somewhat more accurate schemes.

It is seen that an overwhelming mass of data obtained from the most diverse experimental sources is unanimous in yielding the same value for the number of atoms or molecules in a gram-molecule, within the accuracy of measurement. This amazing accumulation of evidence establishes without question the correctness of the Avogadro hypothesis and thus the concept of the atomic and molecular structure of matter. The value of this important number as given by Birge[31] is

$$N_A = (6.064_{36} \pm 0.006) \times 10^{23} \text{ molecules per mole}$$

and

$$N = (2.705_{60} \pm 0.003) \times 10^{19} \text{ molecules per cm}^3.$$

That such accurate and intimate knowledge of this number of entities which cannot be seen or counted should have been gained in three short decades of investigation is indeed a tribute to the method of physical research and to the enterprise of the investigators.

References

1. Hertzfeld, K. F.: *Jahrb. Radioakt. Elektronik*, **19**, 259, 1921. A good comparison of various values of the molecular diameter from this and other data.
2. Perrin, J.: "Atoms," translated by D. L. Hammick, Constable & Co., Ltd., London, 1920.
3. Millikan, R. A.: "The Electron," University of Chicago Press, Chicago, 1925.
4. Rutherford: "Radioactive Substances and Their Radiations," Chap. IV, p. 135, Cambridge University Press, Cambridge, 1913.
5. Millikan: *Loc. cit.*, Chap. VII, p. 148 ff.

6. Einstein, A.: *Ann. Physik*, **17**, 549, 1905; **19**, 371, 1906.
7. Von Smoluchowski: *Bull. Intern. Acad. Sci. Cracovie*, p. 577, 1906.
8. Langevin: *Compt. Rend.*, **146**, 530, 1908.
9. Brillouin, L.: See Perrin: *loc. cit.*, last section Chap. IV.
10. Birge, R. T.: *Rev. Mod. Phys.*, **1**, 1, 1929.
11. Rutherford and Geiger: *Proc. Roy. Soc.*, **A81**, 162, 1908; *Phys. Z.*, **10**, 42, 1909. Braddick and Cave: *Proc. Roy. Soc.*, **A83**, 367, 1928. Regener: *Sitzb. Preuss. Acad. Wiss.*, **38**, 948, 1909.
12. Schottky, W.: *Ann. Physik*, **65**, 51–78, 1921; *Phys. Z.*, **23**, 436, 1922. Hull and Williams: *Phys. Rev.*, **25**, 147, 1925.
13. Dewar, *Proc. Roy. Soc.*, **A81**, 280, 1908; **A83**, 404, 1910. Boltwood and Rutherford: *Phil. Mag.*, **22**, 256, 1911. Hess and Lawson: *Archives Sciences*, **46**, 330, 1918.
14. Hess and Lawson: *Wien. Ber.*, **127**, 405, 1918.
15. Kappler, E.: *Ann. Physik*, **11**, 233, 1931.
16. Johnson, J. B.: *Phys. Rev.*, **32**, 97, 1928.
17. Shaxby: *Proc. Roy. Soc.*, **A104**, 665, 1923. Westgren, A.: *Z. Anorg. Chem.*, **93**, 231, 1915. Svedberg, The.: "Die Existenz der Moleküle." Fürth, R.: *Ann. Physik*, **48**, 410, 1915.
18. Einstein, A.: *Ann. Physik*, **19**, 289, 1906; **34**, 591, 1911.
19. Wadlund, A. P. R.: *Phys. Rev.*, **32**, 841, 1928. Bäcklin, E.: Uppsala Dissertation, 1928. Birge, R. T.: *Rev. Mod. Phys.*, **1**, 40, 1929.
20. Dember, H.: *Ann. Physik*, **49**, 599, 1916. Ramanathan: *Proc. Roy. Soc.*, **A102**, 151, 1922.
21. Millikan: "The Electron." Also, Birge, R. T.: *Rev. Mod. Phys.*, **1**, 1, 1929.
22. Estermann, Frisch, and Stern: *Z. Physik*, **73**, 348, 1931.
23. Meissner and Scheffers: *Phys. Z.*, **34**, 48, 1933.
24. Wolf, F.: *Ann. Physik*, **83**, 849, 1927. Busch, H.: *Phys. Z.*, **23**, 438, 1922. Perry and Chaffee: *Phys. Rev.*, **36**, 904, 1930. Dunnington, F. G.: *Phys. Rev.*, **43**, 404, 1933.
25. Babcock, H. D.: *Astrophys. J.*, **58**, 149, 1932.
26. Houston, W. V.: *Phys. Rev.*, **30**, 608, 1927.
27. Sommerfeld, A.: "Atombau und Spektrallinien," 5th German ed., Chap. V, especially Sec. 3. Paschen: *Ann. Physik*, **50**, 901, 1916; **82**, 689, 1927.
28. Birge, R. T.: *Rev. Mod. Phys.*, **1**, 48, 1929.
29. Birge, R. T.: *Loc. cit.*, p. 54.
30. Birge, R. T.: *Loc. cit.*, p. 55.
31. Birge, R. T.: *Loc. cit.*, p. 58.
32. Virgo, S. E.: *Science Progress*, **108**, 634, 1933.
33. Fletcher, H.: *Phys. Rev.*, **4**, 440, 1914; **23**, 81, 1911. Schmid, E.: *Wien. Ber.*, (IIa) **129**, 813, 1920.
34. Pacini, D.: *N. Cimento*, **10**, 131, 1915. Cabanes, J.: *Compt. Rend.*, **171**, 852, 1920. Fowle, F. E.: *Astrophys. J.*, **40**, 345, 1914.
35. Meibom and Rupp, *Ann. Physik*, **13**, 725, 1932.
36. Kirchner, F.: *Ann. Physik*, **12**, 506, 1932.
37. du Noüy: *Phil. Mag.*, **48**, 264, 664, 1924; **50**, 504, 1925. Langmuir, I.: *J. Am. Chem. Soc.*, **40**, 1361, 1918. Alexander: *Phil. Mag.*, **49**, 663, 1925.

Books Recommended

a. PERRIN, J.: *Loc. cit.* A classic that every physicist and chemist should read.

b. MILLIKAN, R. A.: *Loc. cit.* Another classic of modern science.

c. BLOCH, E.: "Kinetic Theory of Gases," Chap. VII, Methuen & Co., London, 1924. An excellent summary of modern kinetic theory for more popular consumption.

CHAPTER IX

SPECIFIC HEATS AND THE KINETIC THEORY

90. Definition of Specific Heats and the Simple Experimental Facts.—After the perfection of thermometry to a point where physicists could discuss such measurements from a common viewpoint, the next great advance made in the field of heat was the definition of a term which is called the quantity of heat. In the master mind of Black,[1] the obvious interpretation of his measurements connoted to him the existence of an imponderable heat fluid which he could measure. The heat theory based on this connotation is, of course, now completely abandoned, as a result of the interpretation of heat in terms of the kinetic theory which arose scarcely 60 years later. It still remains to interpret this very definite concept, the quantity of heat, in terms of a theory ascribing all heat to the kinetics of gas molecules. Closely associated with the concept of heat quantity is another concept inseparable from it, and without which the definition of a unit of heat quantity is impossible. This quantity is defined as the specific heat. It is the capacity of a body to absorb heat for a given rise in temperature. The unit commonly used in physics is a purely arbitrary one, based for convenience on the most serviceable and common substance used in heat-quantity measurements, to wit, water. The definition of the precise unit is at present much a matter of choice, the convenient unit used being easily convertible into any other unit. This situation arises from the fact that the specific heat of water, *i.e.*, its thermal capacity, varies with the temperature. It is, in general, defined as the heat required to raise 1 gram of water 1°C. at a given temperature which is convenient for the work in hand. Since the change of heat capacity of water with temperature is known, all these may be referred back to the heat necessary to raise 1 gram of water 1°C. at 20°C. This unit of heat quantity is called the gram-calorie. It furnishes a convenient reproducible unit in which to define heat quantity. If with this unit the heat required to raise a gram of any other substance 1°C. be measured, the heat

capacity of that substance relative to water is obtained, or its *specific heat.* This is measured and expressed in terms of calories. A table of values of the specific heats of a number of common substances is given below in order to represent the order of magnitude of the quantities involved.

Substance	Temperature, degrees centigrade	Specific heat at constant pressure	Temperature, degrees centigrade	Specific heat at constant volume
Water	0	1.0094		
Water	20	1.0000		
Mercury	20	0.0333		
Silver	15–100	0.0560		
Aluminum	15–185	0.2190		
Lead	20–100	0.03050		
Carbon (graphite)	11	0.160		
Benzene	10	0.340		
Ice	21– 1	0.502		
Air	20	0.2417	0	0.1715
Hydrogen	.....	3.4020	50	2.402
CO_2	0	0.2010	55	0.1650
Argon	20– 90	0.123	0–200	0.0746
Water vapor	100	0.4652	100	0.340

It is to be noticed that there are in the table two types of specific heats listed—those taken at constant pressure, and those taken at constant volume for gases. The former, designated in what follows by the symbol C_p, is the amount of heat required to raise the temperature 1°C. when the substance is expanding against a constant pressure. Thus this quantity is the heat required to raise the temperature plus that which goes into the work of expanding against the atmospheric pressure. For solids and liquids this is small, and C_p nearly equals the other specific heat, that at constant volume, designated hereafter by C_v. C_v is the heat required to raise 1 gram of the substance 1°C. when the volume is constant, that is, when it does no work. In this sense it measures the true heat capacity of the substance. For gases where expansion is appreciable, C_p contains an appreciable heat expenditure as external work and is distinctly greater than C_v. For solids this is less but is not negligible, as was shown by G. N. Lewis[2] for a number of pure substances.

It is also seen in the table that this quantity varies from 3.4 for hydrogen down to 0.033 for some solids, water having the next highest specific heat to hydrogen. Furthermore, there is, apparently, no regularity in the way in which they vary except that the lighter elements or substances seem to have the highest specific heats. For substances whose densities change rapidly with temperature there is, in general, a rapid change of specific heat with temperature. Thus it might be suspected that, by some correlation of weight or density, the apparent disorder of the values of the specific heats could be changed to show more regularities. In investigating the specific heats of pure elements two Frenchmen, Du Long and Petit, in 1819 observed the important fact that for most solid elements the specific heat multiplied by the atomic weight was a constant, and took on a value of about 6 cal.

TABLE OF ATOMIC HEATS

Substance	Atomic weight	Specific heat	Product
Al	27.1	0.2143	5.80
Pb	206.4	0.0314	6.48
Br	79.76	0.0843	6.33
Fe	55.9	0.1138	6.36
Au	196.7	0.0324	6.37
Cu	63.18	0.0952	6.01
K	39.03	0.1655	6.46
Li	7.01	0.9408	6.59
P	30.96	0.1895	5.87
Hg (solid)	199.8	0.0319	6.37
S	31.98	0.1776	5.68
Ag	107.66	0.0570	6.14
Bi	208.38	0.0308	6.42
C (diamond 10°C.)	11.97	0.1128	1.35
C (diamond 985°C.)	11.97	0.4589	5.49
C (graphite 10.8°C.)	11.97	0.1604	1.92
C (graphite 985°C.)	11.97	0.4674	5.60
B (26°C.)	10.9	0.2382	2.60
B (233°C.)	10.9	0.3663	3.99
B (red heat)	10.9	0.50	5.45
Si (crystalline, 21.6°C.)	28.3	0.1697	4.80
Si (crystalline, 232.4°C.)	28.3	0.2029	5.74

Since a gram-molecule or a gram-atom of a substance is its molecular or atomic weight in grams, this law says that for such simple substances it takes 6 cal. to raise a gram-atom 1°C. Now this at once suggests an interesting conclusion, for by Avogadro's rule (see Sec. 8), the gram-atom of all substances has the same number of atoms. Hence for these elementary solid substances it takes the same amount of heat to raise the atoms in a gram-atom of the solid 1°C., irrespective of the substance. This rule holds well (if the C_p measured is converted to C_v) at ordinary temperatures for all but boron, carbon, and silicon, where the atomic heats are much lower. Investigation shows that these increase their atomic heats, approaching 6 as the temperature is

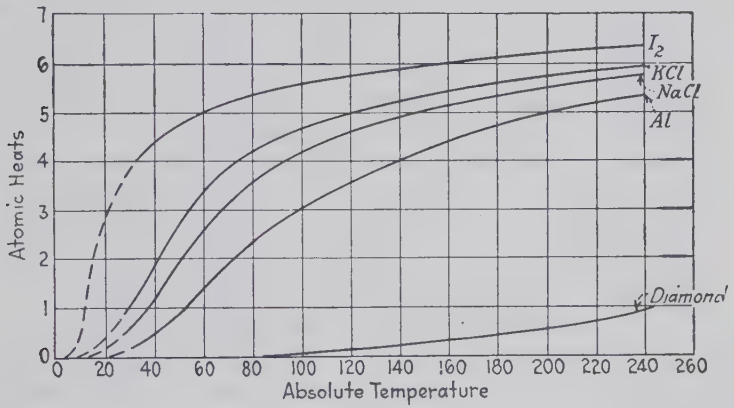

FIG. 55.

raised, while the others all fall below 6 cal. as the temperature falls. At absolute[3] 0 all atomic heats approach 0, as shown by the curves of Fig. 55. At very high temperatures the atomic heat for elements normal at room temperatures begins to increase slowly above the value 6.

If the same criterion be applied to the values of C_p and C_v for gases, the apparent chaos disappears and again a semblance of order appears, with, of course, some deviations. The atomic or molecular weight of the gas multiplied by C_v and C_p gives the following approximate values for three types of gases:

	MC_v, CALORIES	MC_p, CALORIES
Monatomic gases	3	5
Diatomic gases	5	7
Polyatomic gases	6	8

In the diatomic gases certain chemically very reactive gases, such as Cl_2 and Br_2, show distinctly higher values than the rule permits. This holds true also for many of the polyatomic gases, particularly those regarded as chemically reactive at ordinary temperatures. At higher temperatures these approximate constants *all* increase in value, while those deviating at room temperatures tend to conform to the rule as the temperature decreases. Finally, the general rule may be applied to a number of compounds of definite molecular composition. Neumann[4] found that for oxides and sulphides of the form indicated below the molecular heats took on values characteristic of the molecular constitution.

Type of Oxide	Molecular Heat	
RO	11	$= 5.5 \times 2$
RO_2	14.0	$= 4.7 \times 3$
RO_3	18.4	$= 4.6 \times 4$
R_2O_3	26.9	$= 5.4 \times 5$
RS	11.9	$= 5.9 \times 2$
RS_2	18.1	$= 6.0 \times 3$
RCl	12.75	$= 6.4 \times 2$
RCl_2	18.7	$= 6.2 \times 3$
RNO_3	24	$= 4.8 \times 5$
$R(NO_3)_2$	38.2	$= 4.2 \times 9$
RSO_4	26.4	$= 4.4 \times 6$
R_2SO_4	32.9	$= 4.7 \times 7$
RCO_3	21.4	$= 4.3 \times 5$
R_2CO_3	29.1	$= 4.9 \times 6$

Thus there is, clearly, a heat contribution which is roughly proportional to the number of atoms in the molecule, which is, however, influenced in magnitude by certain constitutional differences for specific types of groupings. This remarkable discovery of Du Long and Petit was not only of great use to the chemist in his attempts to establish the correct formulæ for his compounds, but led to an expression for the specific heats which put them into some semblance of order. This order remained unexplained for many years and the kinetic theory offered the first and only explanation. The clue to the meaning of these laws is suggested by the rule of Avogadro that points to the fact that, in elementary solids, the same number of atoms under certain conditions have the same specific heat. Not only have the regularities proved of use, but the very irregularities or deviations have yielded a remarkable service in showing where the classical treatment and understanding ended and the mysterious quantum actions began. In fact, the applications and limitations

of the treatment of specific heats by the kinetic theory furnish one of the most dramatic and fascinating chapters of the kinetic theory and perhaps one of its strongest supports.

91. The Mechanical Properties of Molecules, the Doctrine of Equipartition, and the Classical Values of the Specific Heats of Gases. *a. Mechanical Motions and Definition of Degrees of Freedom.*—As was shown in Chap. II, the energy of the molecules of a gas is definitely related to the absolute temperature and hence to the heat content of a gas. It is therefore clear that the specific heats of gases must be intimately connected with the energy distribution in and among the molecules or atoms of gases. Up to the present, emphasis has, for simplicity, largely been placed on the energy of *translation* of the constituent particles of a gas. This can no longer be done when one is interested in the heat content of a gas, for, since molecules and atoms are mechanical systems, these must also undergo rotations and vibrations. In order to study the energies apportioned to these motions it then becomes essential to analyze the effects of rotation and vibration relative to the energy content of mechanical particles. To this end a brief review of the mechanics of particles must be given.

If one regard a *perfectly rigid* solid body in an attempt to describe its condition or behavior at any instant, one could proceed in several ways. The state or condition of such a body is described completely by its position and its component velocities or, better, momenta at any instant. The position can readily be described by choosing any fixed point on the body and describing its location in space at any time relative to a conveniently chosen set of coordinate axes. In general the description of the motion is more complicated, since the body as a whole not only moves through space, *i.e.*, it undergoes translatory motion as a whole, but in addition the parts of the body move relative to each other, *i.e.*, it undergoes a tumbling or spinning motion. A material simplification in the behavior of a body is achieved in the proper choice of the fixed reference point in the body. The early study of statics showed that in a gravitational field the action of gravity on each element of mass of a complex body could be satisfactorily described by assuming that the whole mass m of the body was concentrated at a single point, the center of gravity or, better, the center of mass of the body. Thus the center of mass might logically be chosen as a

convenient fixed point in the analysis of the mechanical behavior of the body. Under these circumstances the position of the body at any instant is given by the position coordinates of the center of mass at that instant. Again, since the center of mass alters its position in space from one point to another with time, the velocity of the center of mass at any instant can be represented by the rate of change of its position at each instant. This gives the instantaneous value of the translational velocity. In addition, however, the body may rotate or spin about its center of mass. Thus the complete description of the state of the body at any instant is given by the evaluation of the position of its center of mass, the time rate at which this position changes along the axes chosen, and the angular velocities of rotational motion about the axes chosen, through the center of mass. As mechanical space is three dimensional, these quantities can be evaluated in terms of any conveniently chosen independent three-dimensional coordinate axes, *e.g.*, the rectangular Cartesian coordinates X, Y, and Z, or the polar coordinates r, θ, and ϕ. To represent the condition of the body without recourse to any particular system of axes, one may denote the general position coordinates by the letters q_1, q_2, and q_3, which can represent either one of the above axes or any other convenient system. The velocity components of the center of mass will then be dq_1/dt, dq_2/dt, and dq_3/dt.

Actually it is more general and useful mechanically to evaluate the properties of the body in terms of its momentum than its velocity coordinates. If the mass m is independent of velocity as is the case with most gross mechanical systems, the state is adequately described by $m\frac{dq_1}{dt}$, $m\frac{dq_2}{dt}$, and $m\frac{dq_3}{dt}$. Actually Newton's second law of motion is more general in defining force, for it says that force is equal to the rate of change of *momentum*, that is, force is dp/dt, where p, the momentum, itself must be used and not $m\frac{dq}{dt}$, the m being considered constant. As a matter of fact, any and all studies involving the acceleration of masses to velocities comparable with that of light require, as a result of relativity, that Newton's second law be applied in its strict form, since m is a function of velocity or, better, dq/dt. Thus the values of the forces must be derived more indirectly from the energies involved. Hence $\partial p/\partial t$ is given by $\partial p_k/\partial t =$

$-\partial E_P/\partial q_k$ for any coordinate $k = 1, 2, 3$, etc., where E_P is the potential energy, while E_k, the kinetic energy, is related to these quantities by

$$E_k = \frac{m}{2}\left[\left(\frac{\partial q_1}{\partial t}\right)^2 + \left(\frac{\partial q_2}{\partial t}\right)^2 + \left(\frac{\partial q_3}{\partial t}\right)^2\right] = \frac{p_1^2 + p_2^2 + p_3^2}{2m}.$$

Finally for any particular coordinate k, one has from the above

$$p_k = \frac{\partial E_k}{\partial\left(\frac{\partial q_k}{\partial t}\right)}.$$

Again the rotation of the body about its center of gravity can be resolved into three independent components about three appropriately chosen axes. In rotational motion, however, the velocities are the angular velocities ω_1, ω_2, and ω_3, about the three axes chosen and the analogue of mass for rotational motion, the moment of inertia I_1, I_2, and I_3 about each of the three axes, must be used. Thus the rotational state is described by the three products $I_1\omega_1$, $I_2\omega_2$, and $I_3\omega_3$. Hence a complete description of the state of the body at any instant requires a knowledge of the three sets of three independent coordinates, *e.g.*, the position coordinates q_1, q_2, and q_3, the translational momentum coordinates p_1, p_2, and p_3, and the rotational momentum coordinates $I_1\omega_1$, $I_2\omega_2$, and $I_3\omega_3$.

If the translational velocities along the Cartesian coordinates X, Y, and Z, are u, v, and w, and if the mass is independent of velocity, the translatory kinetic energies are $\frac{1}{2}mu^2$, $\frac{1}{2}mv^2$, and $\frac{1}{2}mw^2$ and the corresponding rotational energies are $\frac{1}{2}I_1\omega_1^2$, $\frac{1}{2}I_2\omega_2^2$ and $\frac{1}{2}I_3\omega_3^2$.

In the study of the heat content of a gas, and changes in this quantity, the positions of the centers of mass of the molecules in space are of little importance unless a potential gradient exists, which for the present discussion can be omitted. Hence these coordinates can be left out of consideration. On the other hand the components of translation and of rotation are of paramount importance. In resolving the motions into three independent components to conform to three-dimensional space, these components are mutually independent, so that it is customary to speak of these independent components, or modes, of motion as *degrees of freedom* of motion. Hence it is clear that in general a body has 6 *degrees of freedom of motion*, 3 of translation and 3 of rotation. If a body is a single mass point, *i.e.*, it has no

spatial extent, I_1, I_2, and I_3 are zero so that it will have no rotational momentum and thus it will possess 3 degrees of freedom of translation only. If a rigid body consists of two such mass points only, they will lie on a line and thus have moments of inertia I_1 and I_2 about their common center of mass about axes at right angles to the line of joining the points, but I_3 about the line joining the points will be zero. Hence such a system will have 5 degrees of freedom of motion, *i.e.*, 3 of translation and 2 of rotation. Any other *non-linear* assemblage of mass points making a rigid body will have the full 6 degrees of freedom described above.

In discussing material bodies from the point of view of their mechanical motions, there was at the outset, for the sake of simplicity, added a restriction to these considerations, which in view of the actual structures which one is to study must now be removed. The mechanical body was assumed perfectly rigid. Now it is conceivable that bodies exist which are not completely rigid. That is, the separate mass points composing them may be integrated into a unit such that they have a common center of gravity and move as a whole while they may still be bound together in such a fashion that one of the masses can be displaced relative to the center of mass of the group. If in such a system a displacement occurred in an irreversible fashion, the only change would be that the center of mass and moment of inertia would change at the time of the displacement and thereafter the motion would continue with the changed values, energy having been consumed in the process. If, however, one of the mass points were bound to the system with a spring (*i.e.*, if one had an elastic body), the motion of the body could not completely be described in terms of that for a rigid body. In the case of the elastically bound mass, a relative displacement of the mass point in question and the center of mass of the system would result in a relative vibrational motion of mass point and center of mass. If the amplitude were great, the whole system would undergo marked periodic changes in moment of inertia and center of mass and this would give a most complicated motion to the system. If the amplitude is relatively small, then one may regard the system as essentially unchanged in its fundamental properties and add only the vibrational motion of the two components to the study. Thus in addition to degrees of freedom of both rotation and translation, one must consider the possibility of

degrees of freedom of vibration in a study of the degrees of freedom of motion which a body can assume. As regards the number of degrees of freedom of vibration possible, these must depend on the number of *independent* vibratory motions of mass points involved. In the case of a single mass point there can be no vibration. For two mass points there can be 1 degree of vibration only, the vibration taking place along the line of junction of the mass points. Impacts at right angles to this line merely cause rotation. Three mass points will give 3 degrees of freedom of vibration and in one configuration, 4 degrees. Thus, for any number of mass points, the degrees of freedom of vibration will depend on the number of mass points and their distribution. In general n independent mass points have $3n$ degrees of freedom. Thus it can be stated that for three-dimensional space a single body composed of n mass points will have $3n$ degrees of freedom of motion. Of these, 3 will be used in translation of the common center of mass, 3 will be used in rotation about the center of mass (except in linear configurations), and the remaining $3n$-6 degrees will go to vibration relative to the center of mass. For a linear configuration there are 3 degrees of translational freedom, 2 of rotational freedom, and hence $3n$-5 degrees of vibration. Thus for most configurations of n mass points there are $3n$-6 degrees of freedom of vibration and for linear configurations, the number is $3n$-5 degrees. Hence for the three mass points above there will be either 3 degrees of vibration or 4 degrees for the linear arrangement.

In considering the degrees of freedom of motion which a molecular system can have, it is essential to take stock of the energies involved. For each of the degrees of freedom of translation in a mechanical body the energy is entirely kinetic and is given by $\frac{1}{2}m(\partial q_k/\partial t)^2 = p_k^2/2m$, where k refers to the kth degree of freedom. In the case of rotational motion, the 3 degrees of freedom have each only kinetic energy of rotation in the amount $\frac{1}{2}I_k\omega_k^2$. In the case of vibration the energy is part of the time kinetic and part of the time potential. If the motion is *simple harmonic*, on the average the energy will be one-half kinetic and one-half potential. As the period of oscillation $T = 2\pi\sqrt{m/(f/a)}$, where m is the mass of the particle and f is the force to give a displacement a, then, if $\nu = 1/T$ is the frequency, the potential energy of oscillation is given by P.E. $= \frac{4\pi^2}{2}m\nu_k^2a_k^2$,

if the amplitude is a_k. The kinetic energy is K.E. $= p_k^2/2m$, with P.E. = K.E. and P.E. depending on a_k and ν_k.

b. Molecules as Mechanical Systems.—It is now possible to apply these principles to atomic and molecular systems. The establishment of the nuclear atom by Rutherford showed that for gross mechanical considerations the atom consists of a mass point (nucleus) having, even in the case of the lightest atom, 0.998 of its mass concentrated within a radius of 10^{-12} cm. The remaining 0.002 part of its mass, the electrons, are situated about 10^{-8} cm from the center. For heavier atoms the concentration of mass at the center is even greater for, although the number of electrons increases nearly in proportion to the atomic weight, the higher the atomic weight, the more the electrons are concentrated toward the center. Thus the single atom, as far as mass distribution goes, is essentially a mechanical mass point, if one neglect the very small mass of the more external electrons. Actually it is strictly not a mass point, for it is clear that the electrons should be capable of being given a spin about the nucleus and thus possess a real but minute moment of inertia about it. In practice the electrons do not exhibit a spin about the nucleus for reasons which are best left for later discussion. Hence atoms of the elements in the gaseous state, or monatomic gases, can be considered as essentially composed of single mass points. As such they can have only translatory motion and hence only 3 degrees of freedom of motion.

Where two atoms unite to form a molecule, they unite in such a way that the nuclei are in the neighborhood of an atomic radius apart, *i.e.*, 10^{-8} cm or so. Mechanically for the same reasons as governed the case of the atoms, they may be regarded as two mass points lying on a line but separated by an appreciable distance. They can therefore have 2 degrees of freedom of rotation about axes which are mutually perpendicular and are perpendicular to the line of centers. The small mass of the electrons surrounding the line of centers as in the case of single atoms results in a suppression of rotation or spin about the center line as axis. Thus such diatomic molecules can have 3 degrees of translatory freedom of their common center of mass, and 2 degrees of rotational freedom about it, even though in virtue of their tenuous electronic shells, they may have a space extension in the order of 10^{-8} cm normal to the center line. In addition these atoms are bound together by forces such as were

pictured in Fig. 35 to form the molecule, the attractive forces in the present case being far greater in magnitude than the Van der Waals forces there pictured. It is seen, however, that, if by some external force (such as an impact with another molecule) the atoms are forced together so that r decreases, an oscillation about r_0 will follow. The amplitude of the oscillation will obviously depend on the energy imparted in the impact and may cause but little oscillation or one of such magnitude that the atoms will fly apart, that is, the molecule will dissociate. Theoretically at least, even the slightest impact should suffice to call into being an oscillation or rotation as well as translation, so that one might expect all molecules at all times to show at least a feeble rotation and a feeble vibration. Again, for reasons which later will be revealed, this cannot occur, and, as with the spin of the outer electron shell, there are definite restrictions on the occurrence of the vibrations and rotations which the classical mechanics leads one to expect. In general, however, both rotation and vibration must be looked for.

Hence one can expect of a diatomic molecule 3 degrees of translatory energy, 2 degrees of rotational energy, and 1 degree of vibrational energy.

A polyatomic molecule, it is seen, will correspond to three or more mass points separated again by distances of atomic dimensions. Hence one may at once ascribe to such a molecule 3 degrees of translation, 3 degrees of rotation, and as many degrees of vibrational freedom as there are independent vibrational modes (*i.e.*, $3n - 6$ or for a linear molecule $3n - 5$ where n is the number of atoms in the molecule). Whether all are at any one time operative is again a question which must be reserved until later.

In any case it is clear from the information gained about atomic and molecular structure that atoms and molecules are, from the standpoint of classical mechanics, capable of acting as the mechanical systems which have been discussed.

c. The Theorem of Equipartition.—In Sec. 9 it was shown that if the kinetic interpretation of pressure is accepted, and is combined with Avogadro's rule for mass-point molecules making elastic impacts, it follows that on the average every type of atom or molecule of a gaseous mixture has the same kinetic energy and that this energy is related to the temperature of the gas. Thus, as was shown, if two types of molecules, m_1 and m_2,

of average velocities C_1 and C_2 exist in a gas of pressure p in a volume v at a temperature T, then

$$pv = \frac{1}{3}nm_1C_1^2 = \frac{1}{3}nm_2C_2^2 = RT,$$

where n is the number of molecules in v.

By Avogadro's rule, $n/v = N$ is constant, if p and T are the same. Hence one may write

$$\frac{1}{2}m_1C_1^2 = \frac{1}{2}m_2C_2^2 = \frac{3}{2}\frac{R}{n}T = \frac{3}{2}kT,$$

where $R/n = R_A/N_A = k$ is the value appropriate to *one* molecule, *i.e.*, the Boltzmann constant. This means that the kinetic energy of translation of the molecules m_1 and m_2 in a mixture of gases is on the average the same, or that the kinetic energy is on the average distributed equally among the molecules, whether of different types or not. This is a statement of the law of equipartition of energy for a special case. This law has been tacitly assumed in the early sections of Chap. IV and is discussed in detail in Sec. 36. In this discussion it was shown that it is doubtful whether the law of equipartition can be deduced from purely mathematical physical premises. The suspicion is always present that in assuming elastic impacts and the random nature of the motions, together with large numbers of molecules in such a deduction, one also unconsciously introduces the assumption of equipartition such that the law must follow as a logical result of the reasoning. Be that as it may, equipartition of energy among molecules seems to follow as a logical consequence of the conditions required to describe molecular behavior. Experimentally, as will be seen, it appears to exist among molecules and govern molecular behavior within certain definite limits. At first, attempts to prove it experimentally met with surprising success. Later, exceptions to the law appeared which eventually were all led back to a type of conditions, now termed *quantum conditions*, which place a definite limitation on the operation of the law. For the present, one may omit the discussion of limitations and consider the applications of this principle of equipartition to the case of gases in the classical form.

The assumption of equipartition of energy among different molecular species in a gas was not the only use of the assumption.

In fact, in Joule's simple deduction of the pressure equation from kinetic-theory principles, another assumption involving equipartition was imposed in the conditions placed on the gas to be considered. It was assumed that one *had enough molecules in the volume ABC so that on the average one-third of the molecules were moving parallel to one axis with the same velocity.* In more esoteric derivations of this law, and in the derivation of the distribution of velocities according to Maxwell's method, great care was taken so to choose conditions of equilibrium that the numbers of molecules and the velocities of the molecules were on the average equally likely in all directions in space, and thus one could assert that, on the average, the energy was distributed equally along all three Cartesian rectangular coordinate axes in space. In this case one dealt, for simplicity, with molecular mass points and hence translatory energies only. In Sec. 36, it was, however, also shown that not only did equipartition apply to translation, but that it applied as well to rotation. Finally, the study of molecules in a potential field showed that the energy distribution, and hence equipartition, applied to molecules in equilibrium in the case of potential as well as kinetic energy and that the equilibrium and equipartition thus involved the relation between these two. Thus it is clear that vibrational motion with its kinetic and potential energy must, on classical mechanics, also be considered in the applications of the law of equipartition. Accordingly, the doctrine of equipartition implies that for all types of molecular activity, translation, rotation, and vibration, one must expect the energy on the average to be equally distributed. Hitherto in the text the chief concern has been the distribution of the energy of translation. However, when one deals with the heat absorbed by the molecules and realizes that, mechanically at least, vibration and rotation also occur, the application of equipartition demands that a study be made of the distribution of energy among the various forms of molecular activity. The question thus arises, how can one apportion energy equally among the activities of the molecule. The solution is arrived at very easily as follows. It was seen above that for a molecular species one could write

$$\frac{1}{2}nm_1C_1^2 = \frac{1}{2}nm_2C_2^2 = \frac{3}{2}RT.$$

Now $\frac{1}{2}nm_1C_1^2$ represents the total kinetic energy of the mass-point atoms with the average velocity C_1 and the temperature

T. For one molecule the energy, on the average, is $\frac{1}{2}m_1C_1^2 = \frac{3}{2}\frac{R}{n}T = \frac{3}{2}kT$. Now as was stated, there are *three* degrees of freedom of this translational motion and, if equipartition be invoked, it will be seen at once that each translational degree of freedom of the molecule will have on the average $\frac{1}{3}\left(\frac{3}{2}kT\right) = \frac{1}{2}kT$ ergs of energy of translation. Thus it is seen that equipartition allows one to assign an average amount of energy to each translatory degree of freedom. For a mole of gas, the energy to be assigned to each degree of freedom is

$$\frac{1}{2}N_Akt = \frac{1}{2}R_AT.$$

Expressed in calories $R = 1.9885$, which within the accuracy of many heat measurements can be set as 2 cal. Thus a mole of gas has about $\frac{1}{2}(2T)$ cal. $= T$ cal. of heat energy per degree of freedom of motion.

If other degrees of freedom than translation are present, it is logical to apply equipartition in such fashion that it *allots to each additional degree of freedom the same amount of energy as there is found for a degree of freedom of translation.* Hence one may apply the doctrine of equipartition of energy to molecules of a gas by stating that *to each degree of freedom of motion active on the average there is assigned by equipartition the energy $\frac{1}{2}R_AT$ cal. per mole or $\frac{1}{2}kT$ cal. per molecule.* Roughly speaking this would mean that for each degree of freedom present the energy allotted to that degree of freedom by equipartition is $1T$ cal. per mole at a temperature T.

d. Specific Heats on the Basis of Classical Mechanics and the Theorem of Equipartition.—The total energy, $\bar{E}$ per mole, of a gas it was seen is thus composed of the sum of the energies involved per degree of freedom for translation, rotation, and vibration for all the molecules which are present. Hence one can write

$$\bar{E} = E_T + E_R + E_V,$$

where E_T, E_R, and E_V are the total translatory, rotational, and vibrational energies per mole. Now all gas atoms or molecules

have 3 degrees of freedom of translation. Hence $E_T = 3(\frac{1}{2}R_AT)$ per mole, $E_R = r(\frac{1}{2}R_AT)$ per mole, where r is the number of degrees of freedom of rotation and can be 0, 2, or 3 for atoms and diatomic and polyatomic molecules; $E_V = 2v(\frac{1}{2}R_AT) = 2(3n-6)(\frac{1}{2}R_AT)$ per mole for molecules composed of n atoms with 3 degrees of rotation and $E_V = 2(3n - 5)(\frac{1}{2}R_AT)$ for molecules which are linear and thus have but 2 degrees of freedom of rotation. Here v is the number of degrees of freedom of vibration. The factor 2 in this equation comes from the fact that the energy of vibration is equally distributed between the kinetic and potential forms. Since in equipartition these both share and are equal, the energy must be $\frac{2}{2}R_AT$ for each degree of freedom of vibration. Of course this analysis is classical and assumes that all degrees of freedom present are active. In the case of linear molecules or single atoms, this, however, is nonclassical in that the analysis assumes no spin of the electron shell considering atoms to be single mass points. One accordingly may write

$$\bar{E} = \frac{3}{2}R_AT + \frac{r}{2}R_AT + \frac{2v}{2}R_AT$$
$$= \frac{3}{2}R_AT + \frac{r}{2}R_AT + vR_AT.$$

If $R_A = 2$ cal. per mole, which will suffice for comparison, $\bar{E} = 3T + \frac{r}{2}T + vT$ cal. per mole. The molecular heat, that is, the specific heat per gram-molecule MC_v, where M is the molecular weight and C_v the specific heat at constant volume, is by definition given by $d\bar{E}/dT$. Whence one can write

$$MC_v = \frac{d\bar{E}}{dT} = \left(\frac{3}{2}R_A + \frac{r}{2}R_A + vR_A\right)$$
$$= \left(\frac{3}{2} + \frac{r}{2} + v\right)R_A,$$

and, if R_A is 2 cal., MC_v is approx. $(3 + r + 2v)$ cal. per mole. The specific heat is thus also $C_v = (3 + r + 2v)\frac{1}{M}$ cal. per gram.

As stated before, C_v is the specific heat at constant volume. It represents, therefore, the heat that goes into raising the temperature of the gas alone without any change of internal energy or any consumption of energy for the external work of expansion. One may thus at once predict the classical values of the specific

heats, at constant volume per mole, of gases composed of various types of atomic or molecular combinations.

1. A monatomic gas has $r = 0$ and $v = 0$. Hence one can write approximately $MC_v = 3$ cal. per mole, or accurately $MC_v = \frac{3}{2}R_A$ ergs or cal. per mole, depending on whether R_A is in ergs or calories. This applies to the inert gases He, Ne, Ar, Kr, Xe, Hg and, at high temperatures, to Li, Na, and K.

2. A diatomic gas has $n = 2$. It can have $v = 0$ or $v = 1$.

a. $v = 0$, $MC_v = (\frac{3}{2} + \frac{2}{2})R_A = \frac{5}{2}R_A$ ergs or cal. per mole, or $MC_v = 5$ cal. per mole, approximately. This could apply to gases like H_2, N_2, O_2, NO, CO; to Cl_2 and Br_2 if for any reason $v = 0$. Classically v should not be 0.

b. $v = 1$, 1 degree of freedom of vibration; $MC_v = (\frac{3}{2} + \frac{2}{2} + \frac{2}{2})R_A = \frac{7}{2}R_A$ ergs or cal. per mole, or roughly $MC_v = 7$ cal. per mole. This should apply to any one of the gases above unless, contrary to classical expectations, the vibrations are absent.

3. A polyatomic gas of n atoms has $r = 3$, or $r = 2$ if linear, and $v = 3n - 6$ or $v = 3n - 5$ if linear. Hence one can write $MC_v = \left[\frac{3}{2} + \left(\frac{3}{2} \text{ or } \frac{2}{2}\right) + \left(\frac{2(3n-6)}{2} \text{ or } \frac{2(3n-5)}{2}\right)\right]R_A$ cal. or ergs per mole. If vibrations are absent $v = 0$ and one has $MC_v = (\frac{6}{2})R_A$ or $MC_v = \frac{5}{2}R_A$, which is roughly 6 cal. for a molecule which is not linear and 5 cal. for a linear molecule. In general, however, vibrations from a classical point of view must be present, whence MC_v will be greater than 6 cal. and could be predicted for the classical molecule on the basis given above. Thus one can predict the values of MC_v for classical molecules on various assumptions and compare them with reality.

Actually, C_v is difficult to measure for gases with any degree of precision, due to the difficulty in measuring the small heat quantities involved in heating a gas at constant volume compared to the heating of the containers. Usually C_p, the specific heat at constant pressure, can be measured with greater ease. However, the quantity most easy to measure for a large number of gases is the ratio of $C_p/C_v = \gamma$ using the adiabatic expansion methods, such as that of Clement des Ormes, or, still better, the velocity of sound in the gas by means of stationary waves. Actually C_p and γ have been determined experimentally for most gases so that C_v can be evaluated. It is, however, of use to calculate C_p and γ from theory. In the case of the specific heat at constant pressure, one measures the heat that is spent in the

external work in expanding the gas by a volume ΔV against the pressure p, keeping the pressure constant, plus the heat going into counteracting the Van der Waal forces in expansion in the amount $\frac{a}{V^2}dV$, as well as the heat which goes to increasing the energy of the molecules. Actually the heat going into work against the internal pressure $\int_0^{\Delta V} \frac{a}{V^2}dV$ is entirely negligible because of the small value of a. The work against outside pressure $p\Delta V$ must, however, be included. Since to a first and sufficient approximation $pV = R_A T$, $pdV = R_A dT$. Thus,

$$MC_p dT = d\bar{E} + pdV = d\bar{E} + R_A dT,$$

whence

$$MC_p = \frac{d\bar{E}}{dT} + R_A = MC_v + R_A.$$

Thus one has for MC_p the general relation that

$$MC_p = \left(\frac{3}{2}R_A + \frac{r}{2}R_A + \frac{2(3n-6)}{2}R_A + R_A\right)$$
$$= \left[\frac{5}{2} + \frac{r}{2} + (3n-6)\right]R_A,$$

or roughly

$MC_p = 5 + r + 2(3n - 6)$ cal. per mole for non-linear molecules.

For linear molecules the $3n - 6$ must be replaced by $(3n-5)$. It is seen that MC_p is thus merely about 2 cal. per mole, or, accurately, R_A cal. per mole greater than C_v. Thus, one has for the following gases roughly the following values of MC_p:

1. Monatomic gas: $r = 0, v = 0$ $\quad MC_p = 5$ cal.
2*a*. Diatomic gas: $r = 2, v = 0$ $\quad MC_p = 7$ cal.
b. Diatomic gas: $r = 2, v = 1$ $\quad MC_p = 9$ cal.
3. Polyatomic gas: $r = 3, v = 0$ $\quad MC_p = 8$ cal.

The ratio of the specific heats γ is then given by

$$\gamma = \frac{MC_p}{MC_v} = \frac{\left[\frac{5}{2} + \frac{r}{2} + (3n-6)\right]R_A}{\left[\frac{3}{2} + \frac{r}{2} + (3n-6)\right]R_A} = \frac{5 + r + 2(3n-6)}{3 + r + 2(3n-6)}$$

for non-linear molecules and the same with $3n - 6$ replaced by $3n - 5$ for linear ones. Hence roughly γ takes on the values in the cases cited as follows:

1. Monatomic gas: $r = 0, v = 0$ $\gamma = \frac{5}{3} = 1.666$
2*a*. Diatomic gas: $r = 2, v = 0$ $\gamma = \frac{7}{5} = 1.400$
b. Diatomic gas: $r = 2, v = 1$ $\gamma = \frac{9}{7} = 1.286$
3. Polyatomic gas: $r = 3, v = 0$ $\gamma = \frac{8}{6} = 1.333$
4. Polyatomic gas: $r = 3, v = 1$ $\gamma = \frac{10}{8} = 1.25$
5. Polyatomic gas: $r = 3, v = \infty$ $\gamma = 1.00$.

These predications can at once be summarized in a table[5] which is given on page 445 showing for known gases the predicted and observed values of MC_v, MC_p, and γ.

92. A Brief Statement of the Quantum Theory and Its Elementary Application to the Problem of Specific Heats.—*a. Statement of the Problem.*—A survey of the table shows at once that for monatomic gases the predictions of the application of the theorem of equipartition to the assumed mass-point atoms is borne out surprisingly well for C_p, C_v, and γ. This appears to confirm the theorem of equipartition and the theory. It must, however, be borne in mind that while small, the moment of inertia of the electron shells is not zero in these atoms, and that strictly rotation or spin of electron shells should occur and add its quota to the value of the molecular heat. That it does not indicates *some limitation to equipartition.* Again at $-220°$C., MC_v for H_2 is about 3, the value for a monatomic gas,[6] while at 0°C. it is about 5, the value for a diatomic gas, with $r = 2$ and $v = 0$. The values of MC_v for many diatomic gases show the theory is fulfilled with $v = 0$ and $r = 2$, while at higher temperatures these same gases show that $r = 2$ and v must lie between 0 and 1. Thus there is again *some limitation* on the appearance of equipartition as regards vibration and even as regards rotation in the case of H_2. This restriction as regards vibration begins to disappear at higher temperatures. Finally Cl_2 and Br_2 indicate that $r = 2$ and v is nearly 1, but the values do not correspond exactly. In the case of the more complex gases it is clear that translation and rotation are always present and $r = 3$, while some of the degrees of freedom of vibration are present, but never all of them. Thus MC_v is always greater than the value for $r = 3$ and $v = 0$, but less than the value for $v = 3n - 6$ or $v = 3n - 5$ as the case may be. There is thus definitely a tantalizingly close approximation to the predictions of equipartition but never exact agreement, except for monatomic gases and then not strictly for these. It appears always as if there

Gas	Temp., °C.	MC_v (calc.)	MC_v (obs.)	MC_p (calc.)	MC_p (obs.)	γ (calc.)	γ (obs.)	r	v
He	−255		3.02				1.671		
	18	3.00	3.02	5.00	5.004	1.67	1.659	0	0
Ne	19	3.00		5.00		1.67	1.64	0	0
Ar	15–2500		2.977						
	15	3.00	3.07	5.00	5.07	1.67	1.65	0	0
Hg	275–356	3.00		5.00		1.67	1.66	0	0
Na	750–920	3.00		5.00		1.67	1.68	0	0
H_2	−213	3.00	3.0	5.00		1.67		0	0
	−181	3.00	3.33	5.00	5.338	1.67	1.596	0	0
H_2	0	5.00	4.84	7.00	6.87	1.40	1.407	2	0
		7.00		9.00		1.29		2	1
O_2	20	5.00	5.00	7.00	6.989	1.40	1.399	2	0
	0–2100	7.00	5.84	9.00		1.29		2	1
N_2	20	5.00	5.00	7.00	6.991	1.40	1.410	2	0
	0–2500	7.00	6.02	9.00		1.29	1.37	2	1
CO	18	5.00	5.01	7.00	7.014	1.40	1.398	2	0
		7.00		9.00		1.29		2	1
NO	15	5.00	5.3	7.00	7.26	1.40	1.38	2	0
		7.00		9.00		1.29		2	1
Cl_2	18	5.00	5.90	7.00	8.79	1.40	1.365	2	0
	0–1800	7.00	6.60	9.00		1.29	1.32	2	1
Br_2		5.00		7.00		1.40		2	0
	83–228	7.00	6.88	9.00	8.87	1.29	1.29	2	1
HCl	13–100	5.00	5.09	7.00	7.08	1.40	1.39	2	0
		7.00		9.00		1.29		2	1
CO_2	20	6.00	6.925	8.00	8.89	1.33	1.30	3	0
		12.00		14.00		1.167		3	3
		13.00		15.00		1.153		2	4
H_2O	100–125	6.00	5.33	8.00	6.83	1.33	1.28	3	0
	128–217	12.00		14.00	8.65	1.167	1.33	3	3
N_2O	20	6.00	7.21	8.00	9.24	1.33	1.28	3	0
		12.00		14.00		1.167		3	3
SO_2	20	6.00	7.61	8.00	9.679	1.33	1.27	3	0
		12.00		14.00		1.167		3	3
NH_3	24–216	6.00	6.64	8.00	8.72	1.33	1.30	3	0
	309	18.00		20.00	10.3	1.111		3	6
CH_4	15	6.00	6.49	8.00	8.51	1.33	1.31	3	0
		24.00		26.00		1.083		3	9
C_2H_2	18	6.00	8.44	8.00	10.46	1.33	1.24	3	0
		18.00		20.00		1.111		3	6
C_2H_6	15	6.00	10.3	8.00	12.41	1.33	1.20	3	0
		42.00		44.00		1.047		3	18
$C_4H_{10}O$	16	6.00	30.9	8.00	34.0	1.33	1.10	3	0
		84.00		86.00		1.023		3	39

were a limitation to be applied to the operation of the law of equipartition which restricts its applicability at lower temperatures to periodic motions such as spin, rotation, or vibration. This restriction is furthermore foreign to classical mechanics and in fact is imposed by a necessary extension of classical mechanics

called the *quantum mechanics*. It therefore becomes necessary briefly to sketch the development of the quantum restrictions in order properly to apply them.

b. Introduction to the Quantum Theory.[7]—As a result of the very accurate experimental studies of the distribution of energy among the wave lengths of the continuous spectrum emitted by an incandescent black-body radiator at a temperature $T°$ abs., obtained by Lummer and Pringsheim, Max Planck[8] in 1900 undertook a careful study of the theoretical bases of the deduction of the radiation laws. His study revealed the fact that, while classical theories assuming equipartition and continuous emission and absorption of radiation gave rough agreement, the agreement with experiment was always faulty. The excellence of the experimental data convinced him that the results obtained followed an equation which could never be obtained from the integration of a continuous function and that in fact it could only be obtained by the summation of an infinite series of converging terms. An analysis of the type of series necessary led him to conclude that it would result if the radiant energy were absorbed or emitted in whole multiples of a unit of energy ϵ. In order to make the equations deduced on the assumption of discrete energy quanta ϵ agree with the rigorous portions of the classical equations, it transpired that the value of this new unit of radiant energy ϵ must vary with ν, the frequency of the light, in such a fashion that $\epsilon = h\nu$, where h was a new *universal* constant of value $h = 5.47 \pm 0.008 \times 10^{-27}$ erg sec. This quantity h has thus the dimensions of a moment of momentum as well as energy times time. The remarkable success of this new concept in the field of radiation laws caused Planck to put forth his famous *quantum hypothesis* that radiant energy was emitted or absorbed by matter in whole multiples of a unit $h\nu$. It was not long, however, before the new concept was found to be applicable to other phenomena connected with the relation between radiant energy and matter. In 1905, on the basis of an extension of Planck's law, Einstein[9] derived his famous law of photoelectric action to explain Lenard's observations that the *energy* of the emitted photoelectrons in the photoelectric effect was dependent on the frequency of the light. This law, which reads $\frac{1}{2}mv^2 = h\nu - h\nu_0$, while perhaps deduced on a doubtful basis, was quickly established for X-rays, and in 1915 Millikan[10] accurately proved it for the case of light. In the equation, ν

is the frequency of the incident radiation and ν_0 is the frequency required just to liberate an electron from the surface, *i.e.*, $h\nu_0$ is the work to remove an electron from the surface with zero velocity. By 1907 Einstein[11] had invoked the law to explain the variation of the specific heats of pure crystalline substances with temperature. In 1913 a direct proof of this peculiar quantum restriction on the transfer of energy was given by the work of Franck[12] and Hertz. These two investigators showed that electrons in collisions with atoms lost no appreciable energy unless they were able to impart to the atoms an energy consisting of multiples of a quantum $h\nu$, where ν was a frequency characteristic of each atom and related to the frequency of one of its spectral lines. Almost contemporaneously Nils Bohr,[7,13] in attempting to account for the stability of simple atomic configurations using the newly developed concept of the nuclear atom resulting from Rutherford's researches, was again forced to call upon the quantum concept. He showed that electrons in nuclear atoms could only exist in such stable non-radiating orbits in the atoms whose radii were conditioned by the fact that the moment of momentum of the electrons in the orbit had integral multiples of a quantity $h/2\pi$. The immediate success of this theory in accounting for spectral series established the quantum as more than an hypothesis, and today one may more properly speak of the quantum fact rather than the quantum hypothesis. It thus transpired as a result of the studies of Planck, Einstein, Bohr, and Sommerfeld,[7] that all periodic processes emitting electromagnetic radiations were restricted in the emission or absorption of radiation by definite rules of quantization. The generalized restriction or quantization can be most clearly stated by saying that the periodic system is allowed to take on only such stable states that the integral of the generalized position and momentum vectors equals integral multiples of h. That is, if the motion of the body be depicted in the position and momentum phase plane of one of the coordinates, *i.e.*, the $q_k - p_k$ plane, the paths of the state of the body in the phase plane, *i.e.*, its phase paths, must be restricted to paths such that the area enclosed between any two successive stable phase paths is just h. Another way of stating this would be to restrict the possible stable phase paths of the body in the $p_k - q_k$ phase plane to paths defined by equation $\int_0 p_k dq_k = nh$, where n is a whole number, *i.e.*, 1, 2, 3, 4, etc., and

the subscripts k refer to the kth coordinate of the body's motion. It is to be noted that quantization is applied to each coordinate separately and independently. The justification for this comes from experimental observation of the sharpness of spectral lines, etc., which can occur only if the separate quantizations are independent. Application of this restriction to the case of the simple linear oscillator or vibrator and the simple rotator lead to the following results. For the linear oscillator ΔW, the change in energy between two successive states, is given by $\Delta W = h\nu$ and W_n, the energy of the nth state is $W_n = W_0 \pm nh\nu$. Here W_0 is the lowest energy state of the oscillator and is called the zero-point energy. Quantum studies have finally shown that W_0, the energy at absolute zero, is not zero but is $h\nu/2$. Hence vibrators at absolute zero are not completely at rest but have a zero-point energy.

The analysis of the rotator when quantized leads to the interesting fact that this periodic motion is not quantized in respect to *energy*, but, as Bohr originally showed, its phase paths are restricted to such paths that its moment of momentum in successive paths differs by $h/2\pi$. Hence p_n, the moment of momentum in the nth path or orbit, is given by $p_n = nh/2\pi$, where p_n corresponds to the quantum number n. In general then $2\pi(p_n - p_0) = nh$, where p_0 is the moment of momentum for the lowest state. For a circular orbit $p_0 = 0$. These quantum laws as seen above are applicable independently to each degree of freedom. Thus it is seen that the spinning electron shell, the rotating molecule, and the linear oscillator or the vibrating atom of a molecule have their allowed motions definitely restricted by quantum laws for each degree of freedom, the oscillator being quantized in regard to energy states and the rotator being quantized in regard to its moments of momenta.

Before applying these restrictions to the behavior of atoms and molecules in a gas, one might inquire whether there was any restriction or quantization as regards translatory motion.[15] In this case again one can answer in the affirmative. As before stated, the state of a gas is described by the three position coordinates, q_1, q_2, and q_3, of each of its molecules and by the three momentum coordinates of each of its molecules, p_1, p_2, and p_3. Thus the molecules of a gas can be depicted in a six-dimensional phase space of position and momentum coordinates. Now such phase space can be divided up into cells of the dimensions of

h. But Pauli's[14] famous exclusion principle states that to each elementary cell in phase space there can be only one molecule of a species at one time. In the case of the electrons, the electrons having opposite spin moments are allowed two electrons of opposite spin moments to each cell (see Sec. 101). If the temperature of a gas is very low so that the energies and momenta of the majority of the molecules would be held within relatively narrow limits by Maxwell's law, while at the same time the gas molecules are present in high density, it could occur that there are in the restricted phase space not enough cells of low q and p coordinates to take care of all the molecules. Then Pauli's principle says that all the other molecules that are unable to fill the appropriate cells accorded to them must go to cells of greater p value. Such cells allot more energy to the molecules than the Maxwellian distribution at that temperature warrants and these molecules become *degenerate,* having an energy distribution different from that of Maxwell. At temperatures at which substances are gaseous, and at the densities attainable experimentally, it, however, happens that this case does not occur. Hence in gases there are no restrictions on translatory motions and Maxwell's law is obeyed. It happens, however, that the electron gases in metals, owing to the small electronic mass and the great density of free electrons present, encounter conditions at low temperatures in which the exclusion principle makes most of the electrons degenerate, and it is only at very high temperatures that one approaches a Maxwellian distribution of electron energies in a metal as seen on page 122.

c. Elementary Application of Quantum Principles to Specific-heat Problems.—One is now in a position to apply the quantum restrictions to the problems of the periodic forms of molecular motion to see what the effect on these will be. It is perhaps important first to analyze the problem of the spin of the electron shells about the nucleus in single atoms. For this purpose one can consider the hydrogen atom consisting of a positive nucleus with a single electron at about 0.528×10^{-8} cm distant. The charge of the nucleus and of the electron is $e = 4.77 \times 10^{-10}$ e.s.u. The mass of the electron is 8.99×10^{-28} gram and that of the nucleus is 1.664×10^{-24} gram. The moment of momentum of the electron in its assumed circular orbit is mvr, where v is its linear velocity, r its distance from the nucleus assumed fixed in space, and m is its mass. Quantum laws then set the limita-

tion that the moment of momentum is restricted to values given by the relation $mvr = nh/2\pi$, where n is an integer and h takes on the value 6.547×10^{-27} erg · sec. Now it is convenient to translate this restriction from momentum to energy of rotation, for it is in the energies that the primary interest centers in the case of specific heats. The energy of rotation is $E_r = \frac{1}{2}I\omega^2$, where I is the moment of inertia. In this case $I = mr^2$, and ω is the angular velocity, $\omega = 2\pi\nu = v/r$. Thus $mvr = 2\pi\nu mr^2 = 2\pi\nu I = nh/2\pi$ and $\nu = nh/4\pi^2 I$, so that $E_r = \frac{1}{2}I\omega^2 = \frac{I}{2}(4\pi^2\nu^2) = \frac{n^2h^2}{8\pi^2 I}$ for the nth state of rotation. If $n = 1$,* *i.e.*, for the lowest state of rotation, and since $I = mr^2$, one can evaluate E_r from the data given above. Under these conditions E_r takes on a value of about 2.17×10^{-11} erg. Now the average energy of impact at 0°C. gives 5.66×10^{-14} erg. Owing to the Maxwellian distribution, it is thus seen that at 0°C. it will be a very rare impact indeed that can strike an electronic shell of an atom and impart an energy of spin 500 times the average molecular energy. As a matter of fact, the energy above computed as needed to cause the electron shells of atoms to spin about the nucleus and thus to permit the atoms to take up energy of spin in their lowest state in equipartition is of the same order of magnitude as, if not greater than, the energy required to excite or ionize the atom. Thus it is clearly seen why atoms behave as mass points in the gaseous state and how, by limiting the allowable moments of momenta of the rotating electron by quantum rules, the quantum theory also influences the specific heats. Thus, owing to quantum restrictions, *atoms* will act as single mass points, and the value of their specific heats, up to the highest temperatures open to study, will be the specific heats of bodies with translation only. It is owing to this circumstance that the first apparent agreement between specific heats as predicted by the kinetic theory and those observed was obtained, although careful thought should have shown at once that this agreement was not in keeping with the doctrine of equipartition.

In the case of rotation of *molecules* one again must apply the quantization of the rotator to the problem. Here again the

* In this discussion the effect of only one quantum state, *i.e.*, the first, will be considered for the sake of simplicity. Later the presence of higher states will be discussed.

quantum theory says that a system of mass points can only rotate if the energy of impact available for rotation is equal to E_r, given by the expression $E_r = n^2h^2/8\pi^2I$. In the case of the molecule the only consideration changed by a more rigorous development is the fact that I is now the moment of inertia of the molecule about the axis chosen. To apply this to a specific case, consider the molecule of H_2. Here in the normal state, two atoms (*i.e.*, mass points) of mass 1.66×10^{-24} gram rotate about perpendicular axes whose plane is normal to their line of centers. The distance between the nuclei is 0.75×10^{-8} cm, and the center of gravity is at the center. Hence $r = 0.375 \times 10^{-8}$ cm and $m = 3.32 \times 10^{-24}$ gram so that $I = 4.67 \times$

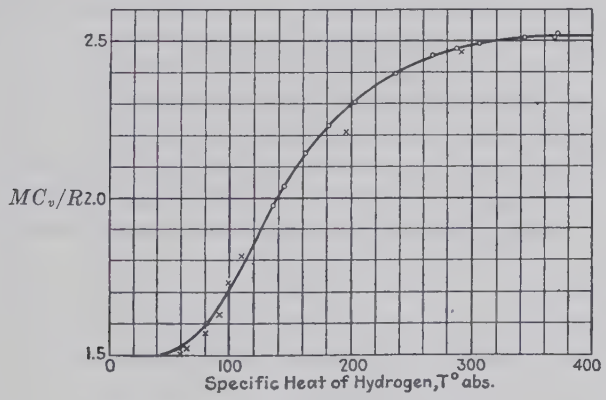

FIG. 56.

10^{-41}. If, again, one takes the state of rotation requiring the lowest energy with $n = 1$, one calculates $E_r = 1.16 \times 10^{-14}$ erg. It is seen at once that the average energy of impact at 0°C. is capable of setting the H_2 molecule into rotation as the energy of impact exceeds the energy required to awaken the lowest quantum state. At 56.6° abs. the average energy of impact is just able to awaken the lowest state of rotation. At 35° abs. the average energy of the molecules together with the conditions of energy transfer at impact and the energy distribution are such that the majority of the H_2 molecules are unable to receive the energy of rotation. Hence one should expect that, at 35° abs., MC_v for H_2 should be 3 cal. and MC_p should be 5 cal. with γ at 1.66. In 1912, Eucken[6] measured γ in H_2 as a function of temperature using the velocity of sound and actually observed a change in MC_p. Later very accurate measurements of East-

man and Cornish[6] confirmed this finding. The results are plotted as circles as MC_v/R against temperature in degrees absolute while Eucken's values are represented by crosses in Fig. 56. Up to 250° abs. the results are in excellent agreement with Dennison's theory to be given later which takes into account values of n for rotation greater than 1. Above 250° abs., agreement is less satisfactory, owing to the change of I due to centrifugal forces of rotation. This thus furnishes an excellent verification of the quantum theory. It is fortunate that H_2, the gas having the lowest value of I, should also have a very low boiling point, for this gas furnishes the only accurate check of the theory from this point of view. The next lightest gas, N_2, has a mass seven times as great as that of H_2. Hence, if the internuclear distances are comparable with those for H_2, I will be several times greater than for H_2 and the cessation of rotation will not occur above the liquefaction temperature. While N_2 and O_2 do show slight decreases in MC_p near their points of liquefaction, the small decrease noted is not sufficiently great to be of much significance. For all other gases, therefore, rotations may be expected to be present and in relatively great amounts.

When it comes to a question of vibration, the rules for quantization showed that a vibrator or linear oscillator can only exist in certain stable states of vibration, whose energy is given by $W_n = W_0 \pm nh\nu$, where n is an integer defining the number of units of vibrational energy $h\nu$ that the oscillator possesses above the ground state W_0. A change in the state of oscillation above the zero-point energy requires then an increment of energy $\Delta W = h\nu$, where ν is the frequency of vibration or oscillation. That is, in order that a degree of freedom of vibration be "awakened" so as to share in equipartition, the molecule must receive the energy ΔW from a single impact. In this case the frequency ν is determined by the binding forces of the molecule in the atom and the variation of this force with its distance from the center of mass. About such forces little can be said *a priori* from the molecular structure. Even the simplest diatomic molecule, the H_2 molecule, has not had the forces and energies accurately worked out on a theoretical basis as a function of the separation of the two nuclei. An idea of the forces acting can be gained from the heat of dissociation of the molecule, which can be determined from thermochemical studies. Fortunately, how-

ever, electrons of atoms and molecules, when moving from one stable state to another, either absorb (if going from a more stable to a less stable configuration) or emit (if going from the less stable to the more stable configuration) electromagnetic radiations which can be detected as X-rays, ultra-violet radiation, visible light, or infra-red radiation. Since the frequency radiated or absorbed is easily determined from spectral analysis, in either emission or absorption, and since $\nu = \Delta W/h$, it is possible by measuring the values of ν observed to determine the energy values of the different states. These energy changes, ΔW, will comprise the difference in electronic energies in the two states, together with any changes in vibrational or rotational states that have occurred. Through the genius of the spectroscopist and the untiring and painstaking work of the countless investigators for the recounting of which there is no space in this text, it has been possible to determine not only the changes in ΔW due to electron transitions but for the vibrational and rotational energies as well. Thus the values of the different rotational and vibrational states have been observed for quite a number of the more stable gaseous molecules. With this knowledge it has been possible to infer the moments of inertia and thus the internuclear distances, as well as the dispositions of the atoms in other than diatomic configurations, from rotational da'a. From the vibrational levels it has been possible to estimate the forces acting at different nuclear separations in diatomic molecules and to infer the heat of dissociation where chemical data were not available. Thus the vibrational frequencies of atoms in molecules are known, and one can at once determine at what temperature of the gas the particular degree of freedom will share in equipartition to its full extent. Needless to say, the values of ν vary over very great ranges, such that in certain molecules it requires temperatures in the thousands of degrees to awaken the vibrational levels, while in other gases, even at room temperatures, these states are active in a large measure if not *in toto*. A glance at the value of MC_v for H_2 and for N_2 will show that, while at room temperatures, v, the vibrational contribution, is strictly zero and $MC_v = 5.0$, this is not the case in the temperature interval from 0 to 2500°C. for H_2 and N_2 where the average MC_v becomes 5.82 and 6.02, indicating a large contribution to energy of vibration due to the awakening of vibrations above 1500 or 2000°C. On the other

hand, the values of ν for the easily dissociated and chemically active molecules Cl_2 and Br_2 show that while at room temperatures the average impact is not sufficient to awaken the degree of vibrational freedom fully, it is nearly so in Br_2 for which $MC_v = 6.88$ since a degree of vibrational freedom should give it an $MC_v = 7.00$. As is seen from the table of computed and observed values for the specific heats of the more common gases, only the most stable and inert gases show no vibration at room temperatures. On the other hand, almost all other gases show the presence of some vibrational energies, but in practically no case does the gas show *all* the vibrational degrees of freedom of which it is capable. For example, ethyl ether is capable of some 39 degrees of freedom of vibration, and, though a reactive molecule chemically, it shows in its value of MC_v that less than 12 of its 39 degrees are fully active. What is more probable is that more of its 39 degrees, but far from all, are partially active. It is accordingly seen that the frequencies of vibration, and thus the energies involved in vibrational motions, lie intermediate between those of the rotations of the molecules and of the electrons themselves. They therefore fall just into the range of energies where temperatures encountered in everyday experience are critically determinative as regards the activity or inactivity of the vibrational mode and thus of the specific heats. Hence, for most gaseous substances, the specific heats can be expected to be a marked function of temperature under ordinary conditions. This is again an excellent demonstration of the influence of the quantum restrictions on equipartition.

Another demonstration of this same limitation lies in the absence of emission spectra in the visible and ultra-violet for gases at normal temperature.[16] The average energy of impact at 0°C. is 5.66×10^{-14} erg, which is equivalent to a frequency of 8.65×10^{13} cycles or a wave length of 3.44×10^{-3} cm. Visible light in the red end of the spectrum has a wave length of 7×10^{-5} cm. Thus it is seen that the average impact will not give rise to visible light. When the temperature is raised to 1200°C., the average energy is 5.4 times as great and the wave length corresponding to the average energy is 1.85×10^{-4} cm. Under these conditions enough of the 2.7×10^{19} atoms in a cm^3 of Na vapor receive an energy of impact capable of exciting the D lines of sodium of wave length about 5.8×10^{-5} cm to make the emission in this wave length capable of detection by the

eye. Thus the flame with Na vapor at this temperature emits the sodium lines. At a lower temperature still, the red line of Li appears, while the bluish lines of K require a higher flame temperature to become visible. Owing to the very sensitive nature of the visual perception, the number of excited atoms, *i.e.*, those in which the energy of impact goes to awakening electronic degrees of freedom is relatively so small that the specific heat of Na vapor would not show a detectable change due to this new source of energy consumption at 1200°C. In fact, in order to have enough energy going into the electronic excitation to make the change in specific heat noticeable in measurement would require temperatures of many thousands of degrees. Hence the excitation of electronic degrees of freedom does not complicate the specific-heat measurements under conditions which are conveniently obtainable in the laboratory.

One more point must be brought out in this discussion of specific heats. All these discussions require that the specific heats be measured under equilibrium conditions. If the vibrations and rotations are of such nature as to liberate electromagnetic waves and these can escape through transparent walls, equilibrium no longer exists. In this sense the impacts become inelastic, for part of the energy given the gas escapes as radiation. Thus the laws of equipartition must be considered as applicable only to cases where equilibrium exists and conditions do not render energy losses to vibration or rotation inelastic.

93. Atomic and Molecular Heats of Solids.—In view of what has gone before in the case of gases, it is a simple matter to explain the law of Du Long and Petit on the kinetic theory. In the solid state, and especially in crystals, it is assumed that the atoms or molecular groups are bound in fixed positions relative to each other. Thus there is not the motion associated with the solid state that characterizes the liquid and gaseous states. Heat motions, obviously, exist, for solid bodies both transmit and absorb heat. Thus they must be capable of taking up the kinetic energy from a gas and, in turn, passing on energy to a gas. A body held in a fixed position, while not free to execute random heat motions, may well move if disturbed. Such a motion will be an oscillation or a vibration about its rest position as center. Since, within certain limits, the forces urging the displaced atom or molecule in a solid back to its initial position may be assumed to obey Hooke's law, the par-

ticles then execute simple harmonic vibrations about their equilibrium positions. Thus the heat motions in a crystal consist of vibrations of the atoms or molecules about their rest positions. Since, on the average, each such degree of freedom of harmonic vibrations has equal amounts of kinetic and potential energies, there are roughly 2 cal. per degree C. associated with each degree of freedom of vibration in a gram-molecule of solid. As there are only 3 degrees of freedom of vibration possible, along the three coordinate axes, the molecular heat should be

$$MC_v = 3 \times R = 6 \text{ cal. per degree C.}$$

Thus Du Long and Petit's law that each molecule or atom has associated with it a given amount of the absorbed energy which goes to raise its temperature at once finds its explanation in terms of the kinetic theory and the law of equipartition. With the exceptions discussed before, and which will be analyzed in what follows, this law holds for the elements very closely. For complex solids the law of Neumann holds. Here it is found that each molecule often does not absorb its full 6 cal., but where certain groupings appear the energy absorbed is less. This finds immediate and simple explanation in the view now held of the crystal structure in the case of complicated molecular groupings. Thus in $CaCO_3$ the crystal is built up of Ca atoms and CO_3 groups. The latter then act as a unit. It is quite plausible to assume that each of the atoms in this CO_3 unit is not free to vibrate in all three of their degrees of freedom. Hence it is to be expected that where the CO_3 group occurs its contribution to the molecular heat may not be 20 units but less, owing to the suppression of some of the vibrational modes in its component atoms. Why some modes are suppressed and others not is explicable on the basis of the quantum theory, for if one of the oxygen atoms is very rigidly bound to the CO_3, and not equally so bound in the group along the three axes, it will require blows of greater energy to set the particular vibration into operation—that is to say, it is possible that at the existing temperature the average kinetic energy is too low to awaken the particular mode of vibration. Hence only those vibrations which are loosely enough bound to be active at the temperature in question should respond, and the energy absorptions will be less by 2 cal. for each such "sleeping" degree of freedom. Of course, since the energy exchanges are statistical, an occasional degree that is normally "sleeping" will absorb. More of these will absorb the higher the tempera-

ture. Thus the molecular heat of such a compound will begin to go up as certain temperatures are approached. This increase will at first be gradual and then more rapid, but in any case more or less continual, due to the continuous value of the energy-distribution function.

The explanation just given for the Neumann law should also apply to all the elements as well. In this case, however, the greater symmetry of the crystal lattices and the equality of the atoms should make the probability of exceptionally strong forces in certain directions less likely. As may be seen from the table on page 428, this is the case. The three elements C, Si, and B, having the highest melting points, however, deviate quite perceptibly and have MC_p well below 6 cal. This is not surprising, since the high melting points of these substances indicate very intense interatomic forces, for the melting points are merely the temperatures where the average kinetic energy of agitation of the atoms becomes comparable with the potential energies of the atoms in the crystal. At this point the interatomic forces cease to be able to hold the atoms in the rigid positions characterizing the solid and the body melts, becoming a liquid. Strong forces mean that the vibrational frequencies of the atoms are high, and thus at room temperatures the average heat impact is not able to impart $h\nu$ to all the different modes of vibration possible. As the temperature increases, this becomes possible and at higher temperatures C, Si, and B all show the normal value for MC_v. As temperatures are lowered, all of the solid elements, and, in fact, all substances, should have decreasing values of MC_v, and at 0° abs. MC_v should be zero, for no mode of vibration can have a frequency so low as to be set into vibration at zero energy.* The accurate study of the decrease of the specific heats of the elements as the temperature was lowered was largely the work of Nernst[3] and his pupils. It was this study which most helped to lead to the explanations of the deviations from Du Long and Petit's law on the basis of the quantum theory.

At very high temperatures MC_v for the elements increases above 6 cal., and, in fact, it is so for the alkali metals at a little

* Actually, as has been indicated in the discussion on quantization, the energy of the oscillators is not zero at 0° abs. as the atoms have a zero-point energy. The vibrations under zero-point energy are, however, those of degenerate atoms, and the distribution is *not* Maxwellian. The value of MC_v is, however, zero at 0° abs.

above room temperatures. This might be ascribed to the absorption of energy into degrees of freedom so far not included. It coincides with the emission of light by the heated solids. The equipartition of energy of motion among the atoms and molecules heretofore discussed, as was stated in Secs. 9 and 91, presupposed that no energy was absorbed into the atoms themselves, that is, it was assumed that the energy was not taken up by individual electrons of the atoms. In view of the work of Franck and Hertz[12] and all of the present-day knowledge of the quantum theory as regards the electronic energy exchanges, it is obvious that at ordinary temperatures it would not be expected that this would occur; at 1000 or 1200°C. there is four to five times the energy of agitation at 0°C., so that the probability of having impacts which can excite some of the lower electronic frequencies begins to be appreciable. It is, therefore, not astonishing that MC_v should increase above 6 cal. at high temperatures.

One more point should be touched on here. In the metallic elements, electrical conduction and even heat conduction received a tentative explanation from the electronic point of view, that is, the parallelism between heat conductivity K and electrical conductivity $1/\rho$ of metals, which was evidenced in the Wiedemann Franz[23] law that $K\rho$ = constant, led to a theory that these conductivities were due to the same agent. On the discovery of the electron, the high electrical conductivity of the metal conductors as against ionic conductors, such as liquids, led to the assumption that the conductivity of the metals was due to the highly mobile electron. Thus heat conductivity was also ascribed to this agent. The conductivity of heat and electricity by electrons led at that time to the assumption of the existence of large numbers of *permanently free electrons* in the metal which were in thermal equilibrium with the atoms of the metal. Certain phenomena, such as the reflection of light by metals, the Peltier effect, the contact potentials, the general photoelectric effect, and the thermionic effect (mentioned in Sec. 45), also seemed to confirm the workers in this belief.[24] On the basis of such evidence, Lorentz[24] worked out an elaborate theory of electronic conduction, which was later extended by Richardson,[24] Drude,[24] Norman Campbell,[24] and others. It led, however, in its extreme form to one conclusion which was not justified by fact. In order to account for optical, conductivity, and Peltier effects, the actual numbers of free electrons present had to be assumed to be very

large, that is to say, they were assumed to be at least comparable in number to the number of atoms present. An alternative to this was that they have mean free paths of excessive length in the metal. While the latter alternative was possible, it did not seem probable at that time. Today it might be considered more likely in view of the apparent transparency of atoms like argon to slow electrons.[25] Thus at that time the assumption of large numbers of free electrons in thermal equilibrium with the metals was made. If this is so, the electrons must, if they are present in the same numbers as the atoms, contribute to the specific heat, that is, MC_v for metals must be increased by 3 cal. for the translational energies of the electrons if there are as many present as there are atoms.

It is of interest to see to what extent this condition holds true. A glance at the values of the atomic heats of the elements in the table of Sec. 90 shows that many of the elements have a heat higher than 6. Others seem to have lower ones. There, furthermore, seems to be no correlation between the electrical conductivity, or "free electron" content, and the excess value of atomic heat as the table stands. G. N. Lewis[26] and Gibson point out that for most of these substances the heat measured is not MC_v but MC_p. While the difference is small, calculation shows it to be appreciable. They obtained data which enabled $C_p - C_v$ to be computed for 15 elements. They found MC_p for iodine to be 6.9, and $MC_p - MC_v = 0.9$. Thus the true MC_v for iodine was 6.0 and not 6.9 cal. The values of $MC_p - MC_v$ calculated by them are given in the following table:

	$MC_p - MC_v$				
Li	0.3	Co	0.1	Sn	0.1
Be	0.2	Ni	0.2	I	0.9
C	0.0	Cu	0.2	La	0.1
Na	0.5	Zn	0.3	Ce	0.1
Mg	0.2	As	0.0	W	0.1
Al	0.2	Se	0.3	Os	0.1
Si	0.1	Zr	0.1	Ir	0.2
S	0.4	Mo	0.1	Pt	0.2
K	0.6	Ru	0.1	Au	0.3
Ca	0.3	Rh	0.1	Tl	0.3
Ti	0.1	Pd	0.2	Pb	0.4
Cr	0.1	Ag	0.3	Bi	0.1
Mn	0.1	Cd	0.3	Th	0.1
Fe	0.1	Sb	0.3	U	0.1

Using these data, they find for 15 elements a mean value of MC_v of 5.9, with the average deviation of 0.09. It is, therefore, shown

that for almost all metals MC_v is nearly 6 and the electrons do not share markedly in the specific-heat contribution. Lewis, Eastman, and Rodebush,[27] however, found that for certain electropositive metals (*e.g.*, Na, K, Cu, and Mg) MC_v rose well above 6 cal. as the temperature went up. In the most electropositive element Cs Dewar[28] showed that, even between the boiling point of H_2 and of liquid air, MC_v was greater than 6 cal.

The conflict between the evidence from specific heats of pure crystalline metallic substances and the electron concept of conduction has been explained since the first edition of this book was written, as a result of Sommerfeld's[15] application of the Pauli[14] exclusion principle and the quantum restriction on translational motions in a free electron gas. As was shown on page 121, and also as discussed in the preceding section in the cases where the density of a gas is very great and when owing to the low temperature, the range of energies and hence momenta of the gas particles (molecules, atoms, or electrons) is very narrow; there are not enough elementary cells in the phase space to take all of the particles at their Maxwellian energies, owing to Pauli's exclusion principle limiting the population of the cells to one atom or molecule, or two electrons with opposite spin. Hence the particles for which there are no phase cells of appropriately low energy enter phase cells of high energy, *i.e.*, they take on energies of higher value than would be accorded to them on Maxwell's law. Such atoms, molecules, or electrons are termed *degenerate*, as they do not partake of equipartition or contribute to such phenomena as specific heat. Now it happens that for gases the densities and temperatures achieved in the gaseous state are not low enough with the large mass involved to cause degeneracy, though in solids very close to absolute zero this occurs. In the case of the free electrons in metals, the densities are 10^4 times as great (one or more free conduction electrons to each atom) and the electron mass is at most $\frac{1}{1850}$ that of the lightest atom. Since the criterion for degeneracy contains the mass of the particle in such a fashion that light particles are more likely to be degenerate, it turns out that the electron atmospheres in most metals are highly degenerate. In fact, it is only above 1500°C. that an appreciable number of electrons in Ag are released from degeneracy, and even here the effect on the specific heat would be negligible. The expression deduced

for the specific heat due to the free electron gas in a metal is as follows. The energy E of the electron gas is

$$E = \frac{3}{5}\mu n + \frac{1}{2}\frac{4\pi^2 mk}{h^2}\left(\frac{\pi}{3n}\right)^{2/3} RT^2.$$

Here n is the number of free electrons per unit volume, μ is given by

$$\mu = \left(\frac{3n}{\pi}\right)^{2/3}\left(\frac{h^2}{8m}\right),$$

h being the Planck constant, m the electron mass, k the Boltzmann constant, and R the gas constant. The quantity $\frac{3}{5}\mu n$ is the *zero-point energy* or the average energy of the totally degenerate electron gas at 0° abs. The equation above thus yields the true value of MC_{v_Q} (the quantum value) for the electron gas as

$$MC_{v_Q} = \frac{dE}{dT} = \frac{4\pi^2 mk}{h^2}\left(\frac{\pi}{3n}\right)^{2/3} RT.$$

The classical value for MC_v for the electron gas, assuming Maxwellian distribution as for a gas of single mass points, is

$$MC_{v_{Cl}} = \frac{dE}{dT} = \frac{3}{2}Nk = \frac{3}{2}R.$$

Hence

$$\frac{MC_{v_{Cl}}}{MC_{v_Q}} = \frac{1.5R}{2.31 \times 10^{-2}R} = 65$$

for electrons of mass m at $T = 300°$ abs. Thus the electron contribution to specific heats in Ag at 300°K is 4.62×10^{-2} cal. per mole, which is entirely too small to be detected experimentally. Hence, owing to electron gas degeneracy at low temperatures while the number of free electrons is of the same order as that of the atoms in the lattice, MC_v for the metal is practically entirely due to atoms and is closely 6 cal. as observed, and not 9, as it would be were the electron gas in the classical condition. Hence there is no conflict on this point any more. This happy interpretation of Sommerfeld has done a great deal to clarify the electron theory of conduction and give explanations of the Peltier, thermionic, and photoelectric effects.

94. Calculation of the Temperature Variation of Specific Heats from the Quantum Theory and the More Accurate Application of

the Quantum Theory to the Specific Heats of Gases. *A. Calculation of the Temperature Variation of Specific Heats from the Quantum Theory.*—It is instructive to study a simple derivation of the equation for the variation of specific heat with temperature. Thus the natural frequencies ν of the atoms may be computed and the value compared with those obtained by other methods. The derivation is also of value, as it indicates how the quantum theory operates in cases already dealt with.

To achieve this, one proceeds as follows. For the sake of simplicity, assume that the oscillator or atom is a linear oscillator describing simple harmonic oscillations. From this and the general law for the distribution of energy, assuming equipartition among the infinite number of values of the energy of oscillation, one obtains, by integration, the average energy for one of the degrees of freedom of the linear oscillator, or the atom. This is an expression which is merely $\frac{2}{2}kT$ for the vibrating atom (see Sec. 36 for further details). The above is merely the application of the distribution law to the case of oscillatory instead of translatory motion. It is then necessary to introduce the quantum conditions before integrating the expression above, which was obtained for the energy before introducing the quantum concepts. Owing to the discontinuous nature of such a quantized energy content, the solution cannot be obtained by integration but must be obtained by summing a series. The new value of the average energy per degree of freedom will then be found to be of a complicated form involving the ratio of the energy quantum and the absolute temperature.

Consider the simplest type of an oscillator, that is, an oscillator which executes simple harmonic motions along a straight line. This might be an atom bound in a crystal. The state of the atom or oscillator is defined by the coordinates x, y, and z of its center mass and u, v, and w of its velocity of translation. From the general law of equipartition of energy, the number of atoms of the solid with these parameters between x and $x + dx$, u and $u + du$, etc., are given by the Maxwell-Boltzmann law of equipartition. This says, in its most general form, that

$$d\eta = Ae^{-2hE}dxdydzdudvdw.$$

In this expression the $2hE$ is equivalent to c^2/α^2 in the expression for the distribution of velocities on Maxwell's distribution law given in Sec. 36. E is, however, the *total energy of a linear*

oscillator and is given by $E = (\frac{1}{2}m\bar{c}^2 + ad^2)$, where $m\bar{c}^2/2$ is the kinetic energy and ad^2 is the potential energy, a being one-half the force constant and d the displacement.

It is simpler to consider the energy along one axis only, since the energies, on the average, are equal along the three axes. This is equivalent to picking 1 degree of freedom of oscillation only. To get this from the above expression one must integrate it for all values of y, z, v, and w. This gives $d\eta_x$, the number of atoms or oscillators with parameters between x and $x + dx$, and u and $u + du$ only, as

$$d\eta_x = A_x e^{-2hE_x} dx du,$$

where

$$E_x = \left(\frac{1}{2}mu^2 + ax^2\right).$$

Putting $h = 1/2kT$, where k is the Boltzmann constant (see Sec. 36), then,

$$d\eta_x = A_x e^{-\frac{E_x}{kT}} dx du.$$

This cannot be integrated in this form, for u and x must be expressed in the same form as E_x, that is, to integrate this equation it must be transformed from an area in the ux plane to an area in polar coordinates in the E_x plane. Since $E_x = \frac{1}{2}mu^2 + ax^2$, one may choose as axes $\sqrt{\frac{m}{2}}u$ and $\sqrt{ax}$. Then $\sqrt{E_x}$ becomes the radius of a circle, and the result is:

$$\sqrt{\frac{m}{2}}u = \sqrt{E_x}\sin\theta$$

$$\sqrt{ax} = \sqrt{E_x}\cos\theta.$$

By means of a Jacobean transformation the area $dudx$ may be transformed into an area in the E_x–θ plane.

$$dudx_\theta = \begin{vmatrix} \sqrt{\frac{m}{2}}\frac{\partial u}{\partial E_x} & \sqrt{\frac{m}{2}}\frac{\partial u}{\partial \theta} \\ \sqrt{a}\frac{\partial x}{\partial E_x} & \sqrt{a}\frac{\partial x}{\partial \theta} \end{vmatrix} \frac{dE_x d\theta}{\sqrt{\frac{am}{2}}}$$

$$\sqrt{\frac{m}{2}}\frac{\partial u}{\partial E_x} = \frac{1}{2E_x^{1/2}}\sin\theta$$

$$\sqrt{\frac{m}{2}}\frac{\partial u}{\partial \theta} = E_x^{1/2}\cos\theta$$

$$\frac{\sqrt{a}\,\partial x}{\partial E_x} = \frac{1}{2E_x^{\frac{1}{2}}}\cos\theta$$

$$\sqrt{a}\frac{\partial x}{\partial \theta} = -\sqrt{E_x}\sin\theta$$

$$dudx_\theta = \left(-\frac{E_x^{\frac{1}{2}}\sin^2\theta}{2E_x^{\frac{1}{2}}} - \frac{E_x^{\frac{1}{2}}\cos^2\theta}{2E_x^{\frac{1}{2}}}\right)\frac{dE_x d\theta}{\sqrt{a\frac{m}{2}}} = -\frac{1}{2}\frac{dE_x d\theta}{\sqrt{a\frac{m}{2}}}.$$

Therefore $$dudx_\theta = -\frac{1}{2}\frac{dE_x d\theta}{\sqrt{\frac{am}{2}}}.$$

For all values of θ, $dudx$ becomes

$$dudx = -\frac{1}{2}\frac{dE_x}{\sqrt{\frac{am}{2}}}\int_0^{2\pi}(d\theta).$$

Hence $$dudx = -\frac{\pi d(E_x)}{\sqrt{\frac{am}{2}}}.$$

From this it follows that

$$d\eta_x = d\eta_{E_x} = Be^{-\frac{E_x}{kT}}dE_x,$$

where $$B = -\frac{\pi A_x}{\sqrt{\frac{am}{2}}}.$$

Now if any value of the energy is equally probable for linear vibration, that is to say, the energy is not quantized or distributed in any other manner, the average energy possessed by a degree of freedom may at once be calculated from

$$\overline{E}_x = \frac{\int_0^\infty E_x d\eta_{E_x}}{\int_0^\infty d\eta_{E_x}},$$

that is

$$\overline{E}_x = \frac{B\int_0^\infty E_x e^{-\frac{E_x}{kT}}dE_x}{B\int_0^\infty e^{-\frac{E_x}{kT}}dE_x}$$

$$= kT,$$

that is, for linear oscillator the energy per degree of freedom is kT. For 3 degrees of freedom it is $3kT$. If it be multiplied by N_A and differentiated for T, then at once $MC_v = N_A\frac{dE}{dT}$ $= 3N_A\frac{dE_x}{dT} = 3kN_A = 3R$, or 6 cal. This is independent of T and is merely the expression obtained for MC_v before

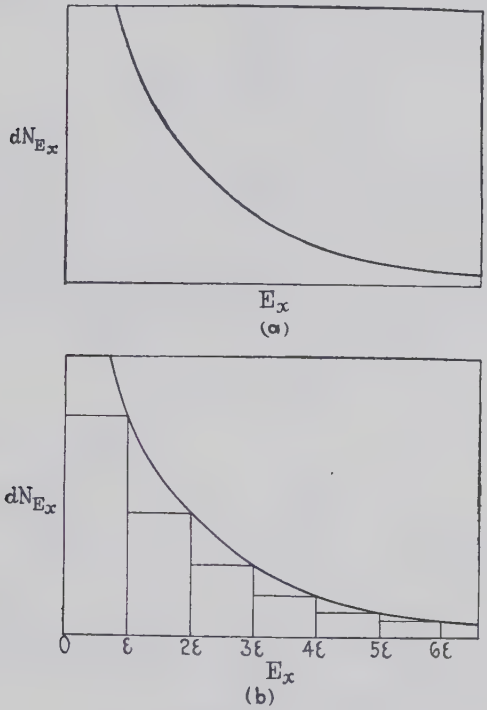

FIG. 57.

on elementary considerations. Now actually, if it is assumed that the energy can only be absorbed in quanta, in which the quanta must be equal to a given value depending on the frequency of the oscillator, it is impossible to integrate in the manner above. The situation may be seen in the two diagrams of Fig. 57. Diagram *a* gives the distribution law for energy E_x among the oscillators, assuming all energies are possible. The average E_x is obtained by the integration process performed above. It is the product $E_x d\eta_{E_x}$ summed up from 0 to ∞, divided by $d\eta_{E_x}$ integrated from 0 to ∞, that is, by the total number of

atoms in each element summed up for all the elements. In the diagram *b* the curve is not continuous, but the total energy content is made up of the various strips $dE_x = \epsilon$ wide and having consecutively the ordinates $d\eta_{E_x}$ given for the particular strip ϵ in question. The E_x is then the sum of an infinite number of the quantities ϵ, of value, respectively, 0, ϵ, 2ϵ, 3ϵ, 4ϵ, etc., the number of atoms having the energy E_x being given by the appropriate value of $d\eta_{E_x}$ for the given energy ϵ, 2ϵ, 3ϵ, 4ϵ, etc. The quantity previously represented by

$$\int_0^\infty d\eta_{E_x} \text{ is now } \sum_0^\infty d\eta_{E_x}$$

$$= B\left[\epsilon e^{-\frac{0}{kT}} + \epsilon e^{-\frac{\epsilon}{kT}} + \epsilon e^{-\frac{2\epsilon}{kT}} + \ldots\right],$$

for the value of $d\eta_{E_x} = Be^{-\frac{Ex}{kT}} dE_x$, and E_x has progressively the values 0, ϵ, 2ϵ, 3ϵ, etc., while $dE_x = \epsilon$, and that represented by

$$\int_0^\infty E_x d\eta_{E_x} \text{ is now } \sum_0^\infty E_x d\eta_{E_x}$$

$$= B\left[0 \times \epsilon e^{-\frac{0}{kT}} + \epsilon \times \epsilon e^{-\frac{\epsilon}{kT}} + \epsilon \times 2\epsilon e^{-\frac{2\epsilon}{kT}} + \epsilon \times 3\epsilon e^{-\frac{3\epsilon}{kT}} \ldots\right]$$

$$\text{Therefore } E_x = \frac{B\left[0 + \epsilon^2 e^{-\frac{\epsilon}{kT}} + 2\epsilon^2 e^{-\frac{2\epsilon}{kT}} + 3\epsilon^2 e^{-\frac{3\epsilon}{kT}} + \ldots\right]}{B\left[\epsilon + \epsilon e^{-\frac{\epsilon}{kT}} + \epsilon e^{-\frac{2\epsilon}{kT}} + \epsilon e^{-\frac{3\epsilon}{kT}} + \ldots\right]}.$$

This leads to the study of the power series obtained by setting $x = e^{-\frac{\epsilon}{kT}}$ and gives an expression

$$\bar{E}_x = \frac{\epsilon x}{(1-x)}, \text{ or } \bar{E}_x = \frac{\epsilon}{e^{+\frac{\epsilon}{kT}} - 1}.$$

To get the specific heat, this must be differentiated with respect to T. Differentiation gives

$$\frac{d\bar{E}_x}{dT} = \frac{\frac{k\epsilon^2}{k^2T^2} e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}.$$

For a gram-molecule, that is, for N_A molecules and for 3 degrees of freedom, one has MC_v for a monatomic gas as

$$MC_v = N_A \frac{3d\bar{E}_x}{dT} = \frac{dE_{N_A}}{dT} = \frac{\frac{3R\epsilon^2}{k^2T^2} e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}.$$

The energy quantum ϵ according to the quantum theory is $h\nu$, where ν is the characteristic frequency of the atoms and h is the Planck constant. Thus one may write that

$$MC_v = 3R \frac{\frac{h^2\nu^2}{k^2T^2} e^{+\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}.$$

It is seen that when $h\nu/kT$ is very large, that is, T is very small, this quantity is nearly 0, and asymptotically approaches 0 as T approaches 0. When kT is large compared to $h\nu$, this quantity approaches $3R$ asymptotically. Since $3R$ is the classical value for MC_v, the equation fits the experimental facts quite well.

This expression, which was first deduced by Einstein[11,16] in 1907,* can be rewritten in a more convenient form, calling

$$\frac{h\nu}{kT} = y = \frac{\Theta}{T};$$

where $\Theta = h\nu/k$, one has

$$MC_v = 3R \frac{y^2 e^y}{(e^y - 1)^2} = 3R \frac{\left(\frac{\Theta}{T}\right)^2 e^{\left(\frac{\Theta}{T}\right)}}{\left(e^{\left(\frac{\Theta}{T}\right)} - 1\right)^2} = 3R\phi\left(\frac{\Theta}{T}\right),$$

where $\phi(\Theta/T)$ is the complex exponential function above, often called the Einstein function. Θ has the dimensions of a temperature and is the characteristic temperature of the lattice. It depends on ν, the characteristic frequency of the lattice, as well as the universal constants h and k, and sets the value of T at which the specific heat reaches the value $3Re/(e - 1)^2$ in its range of values. The Einstein function closely fits the data at higher temperatures but departs seriously at temperatures near 0° abs. Einstein recognized the weakness of his deduction as lying in the assumption that the vibrations were *monochromatic*. Actually, due to the fact that each atom is under the field of force of many other atoms in the crystal, the conditions are not

* An excellent account of this work from which some of the ensuing material was condensed is given by Saha and Srivastava in their book entitled "A Text Book of Heat."[16]

so simple. Nernst and Lindemann[17] attempted to improve on this empirically by assuming that half the atoms vibrated at a frequency ν and the rest at a frequency $\nu/2$. This gives a closer fit than does Einstein's theory. Debye,[18] however, solved the problem quite accurately by a method which is hardly one of kinetic theory. It is of interest at least to indicate the manner in which he proceeded and to give his very important and successful equation. As stated, the individual atom does not vibrate to a single frequency but probably possesses a whole spectrum of elastic frequencies superposed on each other, which can be resolved by Fourier series. Debye disregards the crystalline and atomic structure of the body and uses the classical theory of elasticity to obtain the nature of the vibrations. Such a spectrum consists of a fundamental frequency and overtones ranging from zero to infinity. This of course implies an unlimited number of degrees of freedom of vibration which cannot all exist since the degrees of freedom of vibration are classically restricted to $3N_A$ per mole, where N_A is the number of atoms per mole. To obviate this difficulty, Debye arbitrarily assumed the presence of all frequencies ranging from zero to a limiting frequency ν_m such that the sum of the frequencies from zero to ν_m become equal to $3N_A$. This means that arbitrarily the elastic spectrum is cut off sharply at a definite value of frequency, ν_m. Debye then analyzed the transverse and longitudinal elastic vibrations which travel with well-known velocities derived from the moduli of elasticity. Then, from the velocity and the volume, the number of waves of each kind contained between the values ν and $\nu + d\nu$ can be calculated. Using Planck's evaluation of the mean energy of each wave of frequency ν and counting up the total number of waves, the total energy in the volume V of substance is computed. Setting $h\nu/kT = \xi$ and $h\nu_m/k = \Theta$, differentiating the total energy with respect to T, Debye arrived at the value of MC_v for a monatomic solid as

$$MC_v = 3R\left[\frac{12}{{\xi_m}^3}\int_0^{\xi_m}\frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3\xi_m}{e^{\xi_m} - 1}\right].$$

The quantity in the brackets is known as the Debye function $D(\xi_m)$ and has been evaluated over a range of values of ξ_m. At high temperatures both ξ and ξ_m are small and the integral approaches unity so that $MC_v = 3R$. At very low values of T, ξ_m and ξ are large, the term $3\xi_m/(e^{\xi_m} - 1)$ becomes small,

while e^{ξ} is large unless ν is small. Thus the energy resides largely in small values of ν so that $\xi_m = h\nu_m/k$ becomes infinite essentially in the upper limit of integration. Integration at once yields $MC_v = 3R\frac{12\pi^4}{15}\left(\frac{T}{\Theta}\right)^3$. Thus, since Θ is a constant, MC_v for very low temperatures varies as T^3. This is the famous T^3 law of Debye. Θ can thus be evaluated directly from low-temperature measurements of MC_v. If MC_v be plotted against T, different curves will be obtained for each substance if one use the full equation $MC_v = 3RD(\Theta/T)$, where D stands for the Debye function. If MC_v be plotted against Θ/T, a single curve characteristic for all substances is observed,[19] from which by the use of the value of Θ the curve for MC_v as a function of T for a particular substance can be derived. This relation has been accurately tested for a large number of substances from values of T/Θ ranging from around 0.04 to 2.5. The values of Θ for each substance can be found from experiment, either from the value giving the best fit to experiment for the full curve, or from the value of the T^3 law at low temperatures. Θ can also be calculated from the elastic constants of the substances by the relation

$$\Theta = \frac{h\nu_m}{k} = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\rho^{1/2}\left[\frac{1}{\left(K+\frac{4}{3}n\right)^{3/2}} + \frac{2}{n^{3/2}}\right]^{1/2},$$

V being the volume of the N molecules, ρ the density, K the bulk modulus, and n the modulus of rigidity. In addition Θ can be calculated from the thermal expansion and from the frequency ν_r of the residual rays, assuming $\nu_r = \nu_m$. These agree fairly well with the values obtained by direct measurement from the Debye theory. The agreement is, however, not completely satisfactory, and some substances, such as Hg, Zn, and Cd, depart widely at low temperatures. In addition, it must again be stated that the derivation is in theory to some extent empirical in the introduction of the limiting frequency ν_m and suffers more seriously from the point of view of the kinetic theory in that it overlooks completely the fact that crystals are composed of definite structures of atoms.

B. The More Accurate Application of Quantum Theory to the Specific Heats of Gases.—As a result of what has preceded, it is now possible to consider more in detail how quantization affects

the value of the specific heats. In the elementary discussion of quantum limitations to equipartition in the case of specific heats, it had been assumed that despite the fact that n could be any integral value, provided the energy of impact was great enough to waken that state of rotation or vibration, the value of n was unity. In actual gases n is not unity, for, owing to the distribution of energies among the molecules, there will be some impacts able to impart an energy equal to $n = 1$ to the molecules, fewer impacts able to impart $n = 2$, and still fewer to impart an energy for which $n = 3$. Under any circumstances several values of n are possible, and the higher the average energy of the gas relative to the energy required to activate quanta for which $n = 1$, the more molecules there will be in the higher states. It is also clear that, since the energies of rotation are lower than the vibrational energies, the higher quantum states will be an important factor in rotation at ordinary temperatures. It will be of interest first to discuss the influence of the higher quantum states of rotation on specific heats.

To do this it may be recalled that for the quantization of a rotator the condition imposed was that the energy of rotation in the nth state was given by

$$E_{rn} = \frac{h^2 n^2}{8\pi^2 I}.$$

For the sake of abbreviation $h/8\pi^2 I$ will be designated as A. Here, it is seen that A depends essentially on the moment of inertia of the molecule and on h. Thus one has $E_{rn} = (h^2/8\pi^2 I)n^2 = Ahn^2$. Now the Boltzmann extension of the distribution law (see Sec. 36) enables one to write that the fraction of molecules N_n out of N_A present that have an energy $E_{rn} = Ahn^2$ corresponding to the nth state is

$$N_n = q_n e^{-\frac{Ahn^2}{kT}}.$$

In this equation all terms are familiar except q_n. This is a weight factor which denotes the relative probability of occurrence of the nth state, aside from the considerations of energy. Statistical studies[20] for which there is no place in this text have shown that $q_n = (2n + 1)$. Further study from the viewpoint of wave mechanics[21] has shown that for rotation E_n is not accurately given by $E_{rn} = Ahn^2$ but is more accurately given by $E_{rn} = Ahn(n + 1)$. Thus the equation above becomes

$$N_n = (2n + 1)e^{-\frac{n(n+1)Ah}{kT}} = q_n e^{-\frac{E_{rn}}{kt}}.$$

Accordingly the total energy E_r of the N_A molecules in a mole is

$$E_r = \frac{N_A \sum E_n q_n e^{-\frac{E_{rn}}{kT}}}{\sum q_n e^{-\frac{E_{rn}}{kT}}}$$

which is the total number of molecules multiplied by the average energy of the molecules due to the rotations present, the summation signs being used instead of integrals since the energies E_{rn} are integral values of the energy for which $n = 1$. If Q denote $\sum q_n e^{-\frac{E_{rn}}{RT}}$,

$$\frac{dQ}{dT} = \frac{1}{kT^2} q_n E_{rn} e^{-\frac{E_{rn}}{kT}}, \quad E_r = N_A k T^2 \frac{dQ}{dT}\frac{1}{Q} = RT^2 \frac{d \log Q}{dT}.$$

Hence the specific heat MC_v is given at once by

$$MC_v = \frac{dE_r}{dT} = R\frac{d}{dT}\left(T^2 \frac{d \log Q}{dT}\right).$$

This can be evaluated at once if $A = h/8\pi^2 I$ is known. It is possible to evaluate A from a study of the band spectrum of the molecule, which gives the values of the rotational frequencies emitted in the transition from one rotational state to the next. Again if MC_v be measured as a function of T, then the value of A can be inferred. Thus there are really two ways of obtaining I for the molecule, and, where both can be used and the values of I agree, one may consider the agreement an excellent proof of the theory.

The Einstein equation for the specific heat of solids enables one to calculate the contribution of vibratory motions to the specific heat of gases in a more rigorous fashion[22] than was possible on the simple considerations of Sec. 92. If a single frequency of vibration only is present, as is more nearly the case for the molecule of a diatomic gas vibrating with low amplitude, the Einstein theory can at once be applied. The rough elementary theory of Sec. 92 gave as MC_v for a diatomic gas the expression

$$MC_v = \left(\frac{3}{2}R_A + \frac{r}{2}R_A + vR_A\right).$$

Here r is the number of degrees of freedom of rotation, and v is the number of degrees of freedom of vibration which are respec-

tively 2 and 1 for a diatomic gas. Owing to the fact that the rotations and vibrations are distributed among several quantum states in different amounts corresponding to different values of the quantum number n, one must replace $\frac{r}{2}R_A$ by the rotational expression just deduced taking into account different values of n and one must replace vR_A by the Einstein expression for the average energy of vibration for an oscillator of single frequency ν but having different values of n present which was deduced in part A of this section. Under these conditions the value of MC_v for a diatomic gas becomes

$$MC_v = \frac{3}{2}R_A + R_A E\left(\frac{\Theta}{T}\right) + R_A \frac{d}{dT}\left(T^2 \frac{d \log Q}{dT}\right).$$

Eucken[33] has carried out an extensive comparison of experimental data with theory. Here the frequency ν can be taken from optical measurements. In the case of HCl where the values of ν have been fairly accurately obtained, the agreement is fair. For chlorine also the value of

$$MC_p = \frac{7}{2}R_A + R_A E\left(\frac{\Theta}{T}\right)$$

has yielded satisfactory agreement with experiment, the rotational term being considered as R_A. Thus it has been found that the quantization when more rigorously applied yields values which, despite inadequate data, confirm the theory with considerable success.

A final discussion of the specific heat of hydrogen might be given. This gas has been investigated accurately over a large range of temperatures, and it appeared that no one value of the constant A could be found that fitted the data over all temperatures. Spectroscopic studies of Hori[35] have, however, yielded a definite value of A and hence of $I = 4.67 \times 10^{-41}$ giving a distance between nuclei of 7.5×10^{-9} cm. There had for years been noted a peculiarity in the spectrum of the H_2 which corresponds to that for many other diatomic gases composed of atoms of the same substance. This peculiarity appears in the absence or faintness of alternate lines due to successive values of rotational quantum numbers. This was accounted for by Hund[36] on the assumption of spin moments of the nuclei of the atoms themselves. Such nuclei as H have spin moments and

two types of molecules may be considered, those of the para form in which the nuclei rotate or spin in the same direction (*i.e.*, the spin moments are parallel) and of the ortho form, in which they are antiparallel. The two forms are independent and show considerable reluctance at transforming into each other, the ortho form being three times as frequent in occurrence under ordinary conditions of temperature and pressure as the para

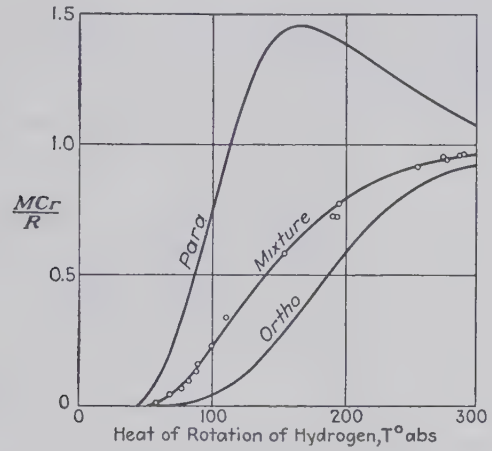

FIG. 58.

form. From the conditions imposed by quantum theory, the quantum numbers of the para molecules should always be even, while those of the ortho form should be odd. This means that in evaluating Q for the rotational contribution to specific heats, two values of Q (Q_p and Q_o for the para and ortho forms) must be computed, one for the even values of n and the other for the odd values of n and the contribution of the ortho form must be counted $\frac{3}{4}$ of the total Q while the para form must be counted as $\frac{1}{4}$. The theory was developed by Dennison[37] in 1927; and with Hori's data Dennison fixed the ratio of ortho to para as 3:1. Beutler has calculated the values of the specific heat MC_v of H_2 as a function of temperature on this assumption, and the agreement is shown in Fig. 58 where the points are Eucken's values and the full curve is the calculated curve. The transformation from the ortho to the para form is very slow, and the relative proportions are temperature dependent. High pressures and low temperatures are conducive to change and by the use of catalyzers, Bonhoeffer and Harteck[39] showed that the pro-

portion of ortho to para while 3:1 at room temperatures, becomes 1:1 at liquid-air temperatures and 0:1 at liquid-hydrogen temperatures. The two forms show different properties, vapor pressures at 20° abs. differing by some 36 mm of Hg in 760. Thus one has another influence governing the quantized values of the specific heat in certain forms of molecules, whose discovery has extended and broadened the understanding of specific heats of diatomic molecules.

In concluding this chapter it will be of profit to indicate the general agreement among some of the values of the characteristic fundamental frequencies of atoms in solids determined from various sources. As assumed in Einstein's theory of specific heats the atoms of a solid have a single characteristic frequency ν, and from the experimental data it is possible to evaluate ν by means of Einstein's theory. As was intimated in the discussion on the nature of molecular forces, ν is determined by the laws of force between the atoms of a solid and these must also determine the melting point, the elastic constants in general, the compressibility, and the expansion coefficients. Each of these by means of theoretical or dimensional reasoning may be related to ν, the assumed single frequency. From the resulting equations it is possible to evaluate the characteristic frequencies in each case. Despite the very approximate nature of the relations used and the fact that the frequencies are not unique, the agreement is surprisingly good. A number of the relations used are given later.

Since ν is a characteristic of the atoms in the crystal structure and is related to the forces of restitution for the atoms in the body, it is not surprising to find that Einstein[29] as far back as 1911 found a relation between ν and the elastic properties of the body. On the assumption that the atom vibrates with simple periodic vibrations (*i.e.*, that it emits monochromatic waves) he derived an expression for

$$\nu_E = \frac{2.8 \times 10^7}{A^{\frac{1}{3}} \rho^{\frac{1}{6}} K^{\frac{1}{2}}},$$

where A is the atomic weight, ρ the density, and K the compressibility of the body. Lindemann[31] assumed that the amplitude of the atomic vibrations in a solid at the melting point is of the order of the distance between the atoms. From this assumption he obtained the following relation between T_S the absolute melting point and the characteristic frequency ν

$$\nu_{T_S} = 2.8 \times 10^{12} \frac{T_S^{1/2} \rho^{1/3}}{A^{5/6}},$$

where A and ρ have the same significance as before. It is seen at once why the light and refractory elements at room temperature depart from the Du Long and Petit law so widely, for with a small A and a large T_S, ν_{T_S} is very great, which makes $MC_v < 3R$ in the equation for MC_v. Finally, E. Madelung[30] and W. Sutherland,[32] independently, found that in certain substances the frequency ν should coincide with the optical frequencies of the atoms. Thus rock salt, sylvin (KCl), and KBr show strong absorption bands in the far infra-red. Together with this they show strong metallic

Comparison of Values of ν for Metals Calculated by Different Methods

Metal	Debye (elastic constants)	Debye (specific heat)	Einstein (specific heats)	Grüneisen (expansion coeff.)	Lindemann (melting temp.)	Haber (ultra-violet spectra)	Austin (compressibility coeff.)	Austin (expansion coeff.)	Residual rays
Ag	4.4	4.5	4.5	4.6	4.4	4.6	4.2	4.4	
Al	8.3	8.3	8.3	7.7	7.8	8.2	7.0	8.1	
Cd	3.5	3.5	....	3.7	2.8	...	2.8	3.5	
Cu	6.8	6.6	6.7	7.1	6.8	7.2	6.0	6.0	
Fe	9.7	9.5	....	8.5	8.3	...	7.0	7.5	
Pb	1.5	1.8	1.5	2.2	1.9	2.5	2.1	1.8	
Diamond	...	...	40.0	...	32.5	...	...	...	
NaCl	...	...	5.9	...	7.2	...	...	...	5.8
KCl	...	...	4.5	...	5.6	...	...	...	4.7

reflection for these same waves. Thus these crystals have atoms which have natural frequencies in this region. These frequencies can be none other than the oscillation frequencies of the atoms in these bodies, for the crystal is known to be composed of a regular lattice in which the metal ion and the anion alternate. Thus as these electric waves have too low a frequency to be electronic in origin, they can come only from the oscillations of the *charged atoms* or *ions* themselves. Since these are the atoms, the atomic frequency ν must be the same as these. Now by repeated selective reflection from a rock salt or other crystal, these waves can be segregated out and their wave lengths measured. Thus one can find ν for the atoms directly by getting the wave length of the residual rays according to Nernst.[34] In the table above are given the values of ν multiplied by 10^{-12} for a number of different

atoms as assembled in a table given by J. B. Austin,[40] to which have been added the values of ν from the Einstein theory of specific heats and at the end the values for NaCl and KCl taken from several different sources including residual rays. The values from the compressibility coefficient given by Austin's computation result from his modification of Einstein's original equation. It is seen that the agreement is in the main much more than one in order of magnitude.

References

1. Black, Mach, E.: "Prinzipien der Wärmelehre," p. 156, Johann Ambrosius Barth, Leipzig, 1896.
2. Lewis and Randall: "Thermodynamics," Chap. VII, McGraw-Hill Book Company, Inc., New York, 1923.
3. Nernst, W.: "Theoretical Chemistry," Chap. III, transl. H. T. Tizard, Macmillan & Co., Ltd., London, 1916.
4. Neumann, F. E.: *Pogg. Ann.*, **23,** 32, 1831. See also Winklemann: "Handbuch der Physik," 2d ed., vol. 3, Heat, p. 190, Johann Ambrosius Barth, Leipzig.
5. "International Critical Tables," vol. 5, pp. 80–84, A. Leduc, McGraw-Hill Book Company, Inc., New York 1929. Landolt-Börnstein: "Physikalisch-chemische Tabellen," 5th ed., vol. 2, pp. 1278–1280, Julius Springer, Berlin, 1923. Also Zweiter Ergänzungsband (vol. 2), p. 218 ff., Julius Springer, Berlin, 1931.
6. Eucken: *Sitzb. Preuss. Akad. Wiss.*, p. 144, 1912; *Ber. Deut. Phys. Ges.*, **18,** 4, 1916. Cornish and Eastman: *J. Amer. Chem. Soc.*, **50,** 627, 1928.
7. Sommerfeld: "Atomic Structure and Spectral Lines," 3d ed., Chap. IV, transl. Brose; Methuen & Co., London, 1928. Ruark and Urey: "Atoms, Molecules and Quanta," Chap. III, McGraw-Hill Book Company, Inc., New York, 1930. Reiche, E.: "Quantum Theory," transl. Hatfield and Brose; E. P. Dutton & Co., Inc., New York, 1923. Saha and Srivastava: "A Text Book of Heat," Chap. XII, Specific Heat of Gases, p. 592 ff., Indian Press, Allahabad, 1931.
8. Planck, M.: *Verh. Deut. Phys. Ges.*, p. 237, 1900; *Ann. Physik*, **4,** 553, 1901; **4,** 564, 1901; **6,** 818, 1901; **9,** 629, 1901.
9. Einstein, A.: *Ann. Physik*, **17,** 145, 1905.
10. Millikan, R. A.: *Phys. Z.*, **17,** 217, 1906; *Phys. Rev.*, **7,** 362, 1916.
11. Einstein, A.: *Ann. Physik*, **22,** 180, 800, 1907; **34,** 170, 590, 1911.
12. Franck and Hertz: *Verh. Deut. Phys. Ges.*, **16,** 10, 1914.
13. Bohr, N.: *Phil. Mag.*, **26,** 1, 476, 857, 1913.
14. Pauli, W., Jr.: *Z. Physik*, **31,** 765, 1925.
15. Sommerfeld, A.: *Z. Physik*, **47,** 1, 1928. Darrow, K. K.: *Rev. Mod. Phys.*, **1,** 90, 1929.
16. Saha and Srivastava: "A Text Book of Heat," Chap. XIV, Indian Press, Allahabad, 1931.
17. Nernst and Lindemann: *Sitzb. Preuss. Akad. Wiss., Berlin*, 494, 1911.

18. DEBYE, P.: *Ann. Physik*, **39**, 789, 1912.
19. SAHA and SRIVASTAVA: *Loc. cit.*, p. 584.
20. SAHA and SRIVASTAVA: *Loc. cit.*, pp. 596, 628.
21. RUARK and UREY: *Loc. cit.*, p. 671.
22. SAHA and SRIVASTAVA: *Loc. cit.*, p. 604.
23. WIEDEMANN-FRANZ LAW: Reiche, E., Marx's "Handbuch der Radiologie," Theory of the Galvanic Property of Metals, part III, Chap. I, p. 281; Chap. II, p. 302; Akademische Verlagsgesellschaft, Leipzig, 1924.
24. RICHARDSON, O. W.: "Electron Theory of Matter," Cambridge University Press, Cambridge, 1914. LORENTZ, H. A.: "Theory of Electrons," Leipzig, 1909. DRUDE, "Lehrbuch der Optik," S. Hirzel, Leipzig, 1912. CAMPBELL, NORMAN, "Modern Electrical Theory," Cambridge University Press, Cambridge, 1913.
25. Sec. 25, Chap. III.
26. LEWIS and RANDALL: *Loc. cit.*, Chap. VII, p. 72.
27. LEWIS, EASTMAN, and RODEBUSH: *Proc. Nat. Acad. Sci.*, **4**, 25, 1918.
28. DEWAR, *Proc. Roy. Soc.*, **A74**, 122, 1904; **A89**, 158, 1913.
29. EINSTEIN, A.: *Ann. Physik*, **34**, 170, 1911; **35**, 679, 1911.
30. MADELUNG: *Nachr. Kgl. Ges. Wiss. Göttingen, Math.-phys. Klasse*, p. 1, 1900; p. 100, 1909.
31. LINDEMANN: *Phys. Z.*, **11**, 609, 1910.
32. SUTHERLAND, W.: *Phil. Mag.*, **20**, 657, 1910.
33. EUCKEN: Wien und Harms, "Handbuch der Experimentalphysik," vol. 8, part I, pp. 442–451, Akademische Verlagsgesellschaft, Leipzig, 1929. Especially Chap. V, parts II and III, and Chap. X, part I.
34. NERNST, W.: *Ann. Physik*, **36**, 426, 1911.
35. HORI, T.: *Z. Physik*, **44**, 834, 1927.
36. HUND, F.: *Z. Physik*, **42**, 93, 1927; *ibid.*, **46**, 349, 1928. HEISENBERG: *Z. Physik*, **41**, 239, 1927.
37. DENNISON, D. M.: *Proc. Roy. Soc.*, **A115**, 483, 1927.
38. BEUTLÉR, H.: *Z. Physik*, **50**, 581, 1928.
39. BONHOEFFER and HARTECK: *Z. Phys. Chem.*, **4B**, 113, 1929; *Naturwissenschaften*, **1**, 182, 1929.
40. AUSTIN, J. B.: *Phys. Rev.*, **38**, 1790, 1931.

Books Recommended

a. BLOCH, E.: "Kinetic Theory of Gases," Chaps. IV, VI, Methuen & Co., London, 1924. A good elementary treatment.
b. REICHE, E.: *Loc. cit.* An excellent review of literature and general summary of the quantum theory.
c. SOMMERFELD: *Loc. cit.* For quantum theory and atomic structure.
d. FRANCK, J.: *Loc. cit.*, vol. 2, 1923. For elasticity of impact and emission of light.
e. CLEMENS-SCHAEFER: "Einführung in die Theoretische Physik," vol. 2, part I, Chap. VIII, Secs. 82, 83, 84, for a detailed discussion of the law of equipartition and its mathematical physical justification.
f. LINDSAY, R. B.: "Physical Mechanics," D. Van Nostrand Company, New York, 1933. This text is particularly adapted for a review of mechanical principles applicable to quantization.

g. SAHA and SRIVASTAVA: "A Text Book of Heat," Indian Press, Allahabad, 1931.

h. RUARK and UREY: "Atoms, Molecules and Quanta," McGraw-Hill Book Company, Inc., New York, 1930.

i. EUCKEN, A.: Wien-Harms, "Handbuch der Experimentalphysik," vol. 8, part I. See *loc. cit.*, reference 33.

j. GEIGER and SCHEEL: "Handbuch der Physik," vol. 23, Chap. I, Julius Springer, Berlin, 1926. W. PAULI: "Quantum Theory," Chap. VII. FRANCK and JORDAN: "Excitation of Quantum States by Impact."

k. HERTZFELD, K. F.: Müller-Pouillet's "Lehrbuch der Physik," 11th ed., vol. 3, part 2, Kinetic Theory of Gases, F. Vieweg und Sohn, Braunschweig, 1925.

l. RICHTMYER, K. F.: "Introduction to Modern Physics," 2d ed., Chaps. VIII, McGraw-Hill Book Company, Inc., New York, 1934.

CHAPTER X

CONTRIBUTIONS OF THE KINETIC THEORY TO ELECTRICAL AND MAGNETIC PROPERTIES OF MOLECULES

I. THE DIELECTRIC CONSTANT OF MOLECULES

95. Elementary Statement of the Problem.—It had long been known that there was a relation between the optical refractive index of a substance and its chemical nature. In fact, Gladstone and Dale[1] as far back as 1858 to 1863, and Landolt[2] found that the refractive index n diminished by unity and divided by the density ρ gave a characteristic quantity associated with each chemical type of atom. This when applied to the atoms of some compounds had marked additive properties. It did not hold for changes of state of aggregation nor did it fulfil the values observed in mixtures very well. An equation was deduced simultaneously in 1880 by Lorenz[3] in Copenhagen and Lorentz[4] in Leyden on a sound theoretical basis which satisfied the condition of being independent of the state of aggregation quite well. It starts out with the assumption that the molecules are spherical electrical conductors. If such molecules find themselves in an electrical field they will have charges induced on them of opposite signs on the two sides of the plane normal to the line represented by the direction of the field and passing through the center, that is, the centers of gravity of the positive and negative electricity present in equal amounts will be shifted from the center of the sphere by the field, so that the molecules act as induced electrical dipoles. Such dipoles would act on the charged bodies producing the field so as to diminish the forces between them, and it is thus that the dielectric constant may be accounted for. Clausius[5] had shown in 1867 that if the fraction of the volume occupied by the substance which is actually occupied by the molecules be u, then the dielectric constant δ is given by an expression $\delta = \frac{1 + 2u}{1 - u}$. This expression will be deduced in a later section. Thus the

fraction of the volume of a gas occupied by the molecules themselves will be given by

$$u = \frac{\delta - 1}{\delta + 2}.$$

For a gram-molecule of substance M, of density ρ, the total volume is $\frac{M}{\rho}$. Then if P_0 is the fraction of the volume occupied by the molecules in a gram-molecule, one may write

$$P_0 = \frac{uM}{\rho} = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}.$$

This P_0 is termed the polarizability and is independent of the density.

Now from the wave theory of light it had been known that δ should approximate n^2, the refractive index, particularly where n^2 could be measured far from an absorption band, or for very long wave lengths when there are no absorption bands in the infra-red. Thus for a gram-molecule where n is the index of refraction, one can write P, the specific refraction:

$$M\frac{u}{\rho} = P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}.$$

The result is an equation representing the relation of the index of refraction to the actual specific volume of the molecule which is supposed to act like a conducting sphere. This should depend on the characteristics of this molecule only and represent its contribution to the refractive index no matter what the state of aggregation. The theory achieved a remarkable amount of success in its applications, and the success achieved may be seen in referring, for instance, to Nernst's[6] "Theoretical Chemistry," Seventh Edition, Chap. VI.

As was seen above in deducing the Lorentz-Lorenz law, which holds surprisingly well, an expression for u in terms of δ, the dielectric constant, was first deduced, on the Clausius-Mosotti theory of dielectrics. This expression *should have the same validity as the expression for the index of refraction which was deduced from it.* Thus since n^2 was assumed equal to δ, the additive law for refractivity should also hold for the dielectric constants δ, that is, P_0 which holds for infinitely long electric waves should be given by $P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$. This is, however, found to be in no sense the case. For some substances the value of P_0 is not at all

constant with the temperature or varying state of aggregation. It also fails for the case of mixtures, and the additive laws found in the case of the index of refraction cannot possibly be applied to some substances. It was at first thought that this was due to the fact that for some substances n^2 did not equal δ, as, owing to absorption bands, the extrapolation of n^2 for visible light did not give the real value in the infra-red (see Nernst, *Loc. cit.*). As investigations in the spectra developed, this explanation of the failure did not seem to agree with the facts and the matter remained unexplained. In 1912, Debye[7] published a paper in which the idea which lay at the basis of his beautiful explanation was expounded. It was further developed in subsequent papers and a masterful account of this will be found in his chapter on the subject in Marx's "Handbuch der Radiologie,"[8] from which a large portion of the subsequent discussion in a simplified form was taken.*

To understand Debye's reasoning, one must return to the underlying Clausius-Mosotti picture of the molecules from which their equation was deduced. The molecules were assumed to be conducting spheres which could not give up their charges on contact but were charged on opposite sides by the inducing field. These by their action led to an expression between u, their total volume, and the dielectric constant δ of the form given before; namely,

$$u = \frac{\delta - 1}{\delta + 2}.$$

For those in a gram-molecule the volume should be $P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$, that is, the actual volume of the spherical conducting molecules in a gram-molecule should be given by P_0. Now from Van der Waals' equation (Sec. 48) one has a quantity b whose volume is four times the total volume of the molecules present. Thus b should equal $4P_0$ calculated from the above equations. Actually, from critical data $b = \frac{V_c}{3}$ or $P_0 = \frac{1}{12}V_c$. From the critical data also $\frac{p_c v_c}{RT_c} = \frac{3}{8}$ (see Sec. 52), so that

$$P_0 = \frac{1}{32}\frac{RT_c}{p_c}.$$

The values of P_0 computed from δ for O_2, H_2, and NH_3 gases are given in the table and compared with the values calculated from

* See also titles *b* and *c* under Books Recommended at end of this chapter.

the critical data. For H_2, $P_0 = \frac{1}{12} V_c$ was used as it was for the first value of O_2. For the second value of O_2 used, as well as for NH_3, the expression

$$P_0 = \frac{1}{32} \frac{RT_c}{p_c}$$

was used as the latter data are better for NH_3.

Gas	P_0 by δ	P_0 critical data
H_2	2.04	4.98
O_2*	4.05	6.20
O_2	4.05	7.83
NH_3	63.0	9.52

* The difference in the figures for O_2 is due to errors inherent in all calculations from critical data (see Sec. 52).

The table is very interesting as it shows first that for H_2 and O_2 the value of P_0 obtained, assuming that the atoms act as conducting spheres, is in as good an agreement as can be expected with observed values of the volumes. For NH_3 this is not the case. The disagreement is striking, being almost one of order of magnitude. Again, the constant P_0 should be additive, as it is for the case of P, using refractive indices. This is found to be the case for carbon and hydrogen in CH_4 and C_6H_6. For H_2, P_0 was 2.04 cm^3, so that for H it is 1.02 cm^3. For CH_4 one calculates, from δ, $P_0 = 7.09$ cm^3, whence if the additive law holds P_0 for carbon should be 3.01 cm^3. Benzene (C_6H_6) leads one to calculate P_0 on the additive law from P_0 for carbon and hydrogen as 24.2 cm^3. The observed value is 27.5 cm^3. Thus for carbon and hydrogen the additive laws for P_0 calculated from δ seem to hold in CH_4 and C_6H_6. For N_2, P_0 is 4.33 cm^3 from δ, so that N has P_0 as 2.16 cm^3 if the additive law holds for N_2, as appears to be the case. Calculating P_0 for NH_3 from these data on an additive law, it comes out 5.22 cm^3. The P_0 as computed from the observed δ is 63 cm^3. Thus again NH_3 fails to obey the additive law, while H, N, C, and O seem to follow it in some compounds.

Finally, if the variation of P_0 with temperature is examined under conditions where the molecules are separated by considerable distances as in a gas or in dilute solutions, it will be found that a large number of them have P_0 constant with temperature, as the theory demands. These substances comprise the whole

group found above that give the values of P_0 from δ which agree with other data, and that follow the additive law, *e.g.*, O_2, N_2, H_2, CH_4, C_6H_6. On the other hand, substances like NH_3, SO_2, H_2O, alcohols, pyridine, etc., which fail to give reasonable values of P_0 from δ and do not follow the additive law, also show a large variation of P_0 with T. Thus for NH_3, P_0 decreases as the temperature increases, as seen in the table below:

T	P_0
292.2	57.57
309.0	55.01
333.0	51.22
387.0	44.99
413.0	42.51
446.0	39.59
448.0	39.50

All these phenomena appeared to Debye to have a common cause, and he asked the question, How can one have a dielectric constant or a portion of it that varies with the absolute temperature? This at once leads one back to the original Clausius-Mosotti explanation of δ. According to them, δ was due to the polarization of electrically conducting spherical molecules. Debye and others investigated this in the light of modern theories of atomic structure and found that the type of action assumed by Clausius and Mosotti for their conducting spheres was also applicable to molecules composed of nuclei with orbital electrons. Debye, however, could imagine no mechanism for this type of polarizing action consistent with modern theory which would account for a temperature variation. If, however, it is assumed that with this polarizability there exist in some of the molecules permanent electrical dipoles the case is entirely different. The precedent for this idea lay in the fact that the chemists had long regarded the electrical charges of substances strongly ionized in aqueous solutions to be segregated even in the molecules. This was required to account for the easy electrolytic dissociation. Thus, for instance, in HCl the H atom was supposed to be positively charged and the Cl atom negatively charged. The HCl molecule has thus a permanent electrical moment as the H and Cl atoms are separated by finite distances from each other in the molecule. With permanent dipoles the whole temperature effect is explained as well as the high non-additive values of P_0. The

idea for this explanation came to Debye from the work of Langevin, who had in 1905 deduced the expression for the magnetic behavior of paramagnetic gases as a function of the temperature, assuming the existence of molecular magnetic dipoles, for if HCl molecules are imagined in a gas the action of a field will be such as to cause the molecules to try to orient themselves in the field. This orientation analogously to the case of molecular magnets in iron in a magnetic field tends to be destroyed by the random heat motions. Thus, although the HCl molecules are free to turn in the field, on the average they are oriented only partially in the field and only a fraction of the moment is effective. This could be expressed by the moment multiplied by the cosine of the average angle of orientation in the field. The higher the temperature the less the orientation and hence, as the temperature increases, the value of δ, and so the apparent value of P_0, should decrease. Again, the Clausius-Mosotti equation allows one to calculate only the induced portion of P_0. Thus the values of P_0 due to the induced electrification of separate atoms in a compound should really be less than values of P_0 calculated from a δ where part of this quantity is due to permanent moments. This explains the non-additive nature of the values of P_0 for such compounds. While N and H separately have a small additive P_0 due to induced electrification of the Clausius-Mosotti type when they unite to form NH_3, there is a new grouping with a large permanent dipole moment due to the segregation of the charges in this particular type of molecule. Other compounds of H and N which did not have this could conceivably have a δ and hence a P_0 where the H and N P_0 values combined purely additively and were of a simple induced nature. Most compounds have a P calculated from the index of refraction which is nicely additive, since, because of the very high frequency of the light vibrations, the slow orientation of the permanent molecular dipoles in the field cannot occur. Hence here mostly the purely induced dielectric constants which are nicely additive are dealt with. In certain cases where the frequencies of the light waves approach frequencies of dipole rotation in the infra-red this no longer holds and the additivity then begins to break down.

This beautiful explanation of the paradoxical situation of the two equations of $P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$ and $P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}$, where the second equation held while the one from which it was derived

failed, merits treatment in this book because of its relation to the kinetic theory. In the succeeding sections the Clausius-Mosotti equation will be deduced and the Debye calculation for the temperature variation of δ will be given. Section 97 will give the beautiful quantitative agreement between theory and experiment. In Part II, the treatment of the magnetic properties of gases from a similar point of view will be given.

96. Theory of the Variation of Dielectric Constant with Temperature. *a. The Deduction of the Clausius-Mosotti Law.*— Consider a region in free space with no material present and produce an electrical field E in this region; the field produced has the intensity E, that is, if one represent it by the number of lines of force per cm^2 normal to the direction of these lines, there will be E lines of force per cm^2. If, now, one place matter in this space, the field intensity will no longer be E, but it will have the value D. D is, however, related to E in a simple manner. Owing to the presence of induced electrical charges in the dielectric, the added lines of force can be treated as coming from the two ends of the volume considered, the ends being chosen normal to the lines of force, that is, the action of this region filled by matter can be imagined as being replaced by two condenser plates with a charge density at the two ends of the volume. This new charge gives lines of force which add to the field E initially existing. If unit volume is considered, these charges may be designated as $\pm P$. Hence, numerically, each unit volume will contribute $4\pi P$ new lines to the field E. Thus D, the dielectric displacement, is given by

$$D = E + 4\pi P,$$

where P is called the polarization. Now P is proportional to E in certain cases, for P is caused by E. Thus $P = KE$, where K is the electrical susceptibility. For the cases where this holds then

$$D = E(1 + 4\pi K).$$

This may be written in a different form, to wit, $D = \delta E$, where $\delta = 1 + 4\pi K$ and is known as the dielectric constant. It is the same quantity by which the force between two electrified bodies in a medium is reduced by the polarization of the medium. Thus it is δ which is measured experimentally, and the quantity K must be derived from it.

All the above considerations apply to the case of a homogeneous medium filled uniformly with matter of dielectric properties. Actually, matter is made up of molecules whose total volume may make up only a fraction of the total volume. The question of interest is how these molecules affect the dielectric constant, and what can be learned about the molecules by a study of their dielectric constants. It could be assumed that for any one molecule the relations of the last paragraph were applicable. This molecule does, however, not find itself in an isolated space in a field E devoid of matter. It is, in fact, surrounded on all sides by molecules, each of which is polarized and each of which consequently contributes to the field acting. The field in which a molecule finds itself is not now E, but a field F. This F may also be considered proportional to E, so that one may write

$$F = E + \nu P.$$

This field will be designated as the *inner field*. The constant factor ν is called the constant of the inner field. It is a pure number which replaces the 4π in the equation above. Its value depends on the nature and distribution of the molecules. Calculations for which there is no space in this book make it possible to determine ν. For a more complete treatment, refer to H. A. Lorentz,[9] and a complete summary of the literature will be found given by Born.[10] For spherical molecules which constitute the corners of a regular molecular (or atomic) space lattice, or for such molecules which are distributed completely at random in space, (*e.g.*, as in a gas or a liquid), this factor ν is $\frac{4\pi}{3}$. Thus instead of D one now uses the inner field F, given by $F = E + \frac{4\pi}{3}P$ for cases which are of interest in the questions raised.

In the electrical case saturation as observed in ferromagnetic substances is hardly detectable.* Thus it may be assumed that a molecule in an inner field F will acquire a moment m whose average value with time $\bar{m}$ is proportional to F. Hence $\bar{m} =$

* The reason for this is that the electric fields are so feeble compared to the atomic electrical fields that the polarization produced is very slight, thus, as in magnetism, one can assume proportionality for weak fields through narrow ranges. Furthermore, the orienting action of the weak electrical fields on molecular dipoles in gases and liquids is too slight with the violent heat motions to give saturation.

γF. If there are in unit mass of the substance z molecules, and if the density is ρ, then

$$P = \rho z \bar{m} = \gamma \rho z F.$$

As, however,

$$F = E + \nu P$$

it follows that

$$P = \frac{\rho z \gamma}{1 - \nu \rho z \gamma} E,$$

and

$$K = \frac{\rho z \gamma}{1 - \nu \rho z \gamma},$$

and therefore

$$\delta = 1 + 4\pi K = \frac{1 - (\nu - 4\pi)\rho z \gamma}{1 - \nu \rho z \gamma}.$$

These equations relate K and δ to ν and the polarizability of a single molecule γ. One may also put this in the form

$$\frac{\delta - 1}{\delta - \frac{\nu - 4\pi}{\nu}} = \nu \rho z \gamma,$$

by solving for $\rho z \gamma$. For the case where $\nu = \frac{4\pi}{3}$ the solution then becomes

$$\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3} \rho z \gamma.$$

If γ, the polarizability, is a constant independent of pressure or temperature, the quantity $\frac{\delta - 1}{\delta + 2}$ is by the equation proportional to the density. Where $\frac{\delta - 1}{\delta + 2}$ is not proportional to the density, that is, where $\frac{1}{\rho} \frac{\delta - 1}{\delta + 2}$ is not a constant, it is to be inferred that γ, the polarizability, varies with the temperature or pressure. That this actually occurs was noted in the Introduction, for δ is a function of the temperature. It was the study of this temperature variation which led Debye to the assumption of molecular dipoles. The above expression is the Clausius-Mosotti law.* To obtain the Lorenz-Lorentz expression from this, it

* In the deduction here, however, the conducting sphere hypothesis is absent. Clausius and Mosotti deduced the law and calculated the factor $\nu = \frac{4\pi}{3}$ for the special case of a conducting sphere. The deduction here is correct for any body with positive and negative charges that are relatively mobile and for the cases of random or special spatial distribution.

need only be remembered that $\delta = n^2$, where n is the index of refraction, if one is far from an absorption band and at infinite wave length. Thus one can write

$$\frac{1}{\rho}\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3}\gamma z,$$

and

$$\frac{1}{\rho}\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\gamma z,$$

as the Clausius-Mosotti and Lorenz-Lorentz equations. To make them more useful, both sides may be multiplied by the molecular weight M. Then

$$\frac{M}{\rho}\frac{\delta - 1}{\delta + 2} = \frac{4\pi}{3}\gamma N_A,$$

and

$$\frac{M}{\rho}\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\gamma N_A,$$

where N_A, the Avogadro number, is Mz. Thus the molecular refraction is a constant times the molecular polarizability. Call $\frac{4\pi}{3}\gamma N_A$ as deduced from the refractivity P, and the value deduced for the dielectric constant (*i.e.*, for infinitely long waves) P_0; then

$$P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho},$$

and

$$P = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho}.$$

The P should be equal to P_0 if for high-frequency waves and infinitely long waves δ is a constant independent of temperature. As was stated before, the law for polarizability seems to hold for fast vibrations (*i.e.*, for the equation for P), but does not hold for the equation from which this was deduced (*i.e.*, the P_0 equation).

The quantity P_0 has the dimensions of a volume. Its meaning in this sense becomes evident if one takes the earliest Clausius-Mosotti theory which assumes the molecules as conducting spheres of radius a, which do not lose their charges on contact. The moment m of such a sphere in a field F is then merely

$$m = a^3F.$$

Since $\bar{m} = \gamma F$, one obtains for this case

$$\gamma = a^3;$$

whence,

$$P_0 = \frac{4\pi}{3} N_A a^3.$$

But $\frac{4}{3}\pi a^3$ is the volume of a sphere of radius a, and N_A times this is simply the total volume of these supposed spherical molecules in a gram-molecule, that is, $P_0 = \Omega = \frac{b}{4}$, where Ω is the volume of all the molecules in a gram-molecule, and b is the b of Van der Waals' equation for a gram-molecule. As will be seen by referring to the preceding section, these predictions are fulfilled for certain substances but fail badly for others. Since, again, Ω is a constant for each type of atom, it should follow an additive law for compounds. It is found that this holds for the same substances for which P_0 computed from δ agrees with the values from Van der Waals' equation, but not for the others. The Lorenz-Lorentz equation fits fairly well for all substances in spite of the fact that it was derived from the Clausius-Mosotti law for δ which breaks down. It was the fact that the substances for which the Clausius-Mosotti law fails show a temperature variation of Ω (*i.e.*, for which γ is not independent of pressure and temperature) that Debye used in discovering the clue to the discrepancy.

b. The Temperature Variation of the Dielectric Constant.—On the basis of the preceding difficulties, Debye began to investigate the cause of a temperature variation of γ and hence P_0. The first question investigated was whether the modern views of atomic structure can cause the modifications required. The atom or molecule is considered a dynamical system of charges. If the average positions of the charges are disturbed by some external force, these charges endeavor to return to their average positions again. Investigations show that it makes no difference whether these charges are dynamical or static systems. It was also found that the sharing of the heat motions of the molecules by the electronic charges would make no difference in the law of force. As is seen (Sec. 92), this does not occur in molecules at ordinary temperatures, so that even if it did have an effect the question would not be solved. Another way out might be to assume that the electrons are unsymmetrically bound to their rest positions as a second approximation, so that the potential energy of the charge on a displacement ξ would be represented

by $\frac{f}{z}\xi^2 + \frac{g}{z}\xi^3$, where f and g are constants of the elastic forces. Then if the electrons shared in the heat motions, the change of dielectric constant with temperature would result. As said before, however, such an interpretation is contrary to the verdict from specific-heat considerations, and so will have to be discarded. For solids where thermal expansions change the elastic forces, and hence could change the displacements, these considerations would, of course, be applicable.

If it be assumed that the dielectric constant has, in part, another origin than the simple induced dipoles due to the displacement of the charges by the field, the whole problem is simplified. If, for instance, certain molecules like HCl have permanent dipoles present, then their dielectric constant is composed of two types of action. There is the usual further separation of the charges by the field, which has no temperature effect, and was calculated by the Clausius-Mosotti relation. This can, for the present, be ignored. The fixed dipoles in the molecules which are oriented in all directions because of thermal agitation suffer torques in the electrical field, that is, they tend to set themselves parallel to the field. This orientation is continually destroyed by the heat impacts. But, on the average, there is a resultant component of these dipoles in the field and they act to increase the dielectric strength of the material, that is, they contribute to the polarizability of the molecules. The higher the temperature, and hence the thermal agitation, the less this orientation. Thus the polarizability must decrease as temperature increases. To investigate this, one may neglect the Clausius-Mosotti type of action, and consider the charges as undisplaceable. Let the position of one of the e_i charges composing the molecule be given by its coordinates ξ_i, η_i, ζ_i along the axes x, y, z of a coordinate system in the molecule. The molecule in an electrical field of potential ϕ will have the potential energy $u = \sum e_i \phi_i$. Inside the molecule, in general, it will be possible to determine the ϕ_i in terms of its development in a power series of the coordinates ξ, η, ζ. By taking only the linear terms of these expressions, the assumption of a homogeneous field inside the molecule is introduced. If this assumption is made for simplicity, then

$$\phi_i = \phi + \xi_i \frac{\partial \phi}{\partial x} + \eta_i \frac{\partial \phi}{\partial y} + \zeta_i \frac{\partial \phi}{\partial z},$$

where ϕ and $\partial\phi/\partial x$ are taken relative to the origin of the coordinate system of axes chosen. For the energy u then

$$u = \phi\sum e_i + \frac{\partial\phi}{\partial x}\sum e_i\xi_i + \frac{\partial\phi}{\partial y}\sum e_i\eta_i + \frac{\partial\phi}{\partial z}\sum e_i\zeta_i.$$

If the molecule as a whole is uncharged, the $\phi\sum e_i$ term is 0, and the following three terms represent the scalar product of the field strength F and the electrical moment m. Thus without displacement of charges there is, in general, a potential energy

$$u = -(mF).$$

To compute the temperature effect, all that is needed is to assume molecules with a fixed moment of absolute value μ. From the classical kinetic theory, there will be equilibrium between the potential energy of these dipoles in the electrical field and the kinetic energy of agitation. Thus the number of molecules which have a potential energy of the value u, that is, whose potential energy in the field is $u = -mF = -\mu F \cos\theta$ (where θ is the angle between m and F), is given by the Maxwell-Boltzmann law (see Sec. 36) as

$$Ae^{-\frac{u}{kT}}d\Omega = Ae^{\frac{\mu F\cos\theta}{kT}}d\Omega,$$

where $d\Omega$ represents the space-angle element of volume characterizing this energy. Thus each molecule has a moment $\mu\cos\theta$ in the direction of the field and the distribution law (see Sec. 36) gives one the number of molecules having moments for each value of θ. The average moment, that is, the moments for all the different angles of orientation averaged in terms of their probability of appearance, can be found very easily as

$$\overline{m} = \frac{\int_0^\pi e^{\frac{\mu F}{kT}\cos\theta}\mu\cos\theta d\Omega}{\int_0^\pi e^{\frac{\mu F}{kT}\cos\theta}d\Omega}.$$

The integration may easily be performed as follows. The elementary volume $d\Omega$ is in this case given by $d\Omega = 2\pi\sin\theta d\theta$. Let $\zeta = \cos\theta$ and $x = \mu F/kT$. Then

$$\frac{\overline{m}}{\mu} = \frac{\int_{-1}^{+1} e^{x\zeta}\zeta d\zeta}{\int_{-1}^{+1} e^{x\zeta}d\zeta}.$$

Integration of numerator and denominator with subsequent simplification gives

$$\frac{\overline{m}}{\mu} = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x} = L(x).$$

This function, represented in Fig. 59, plotted against x is named the Langevin function, after P. Langevin, who first applied it in explaining the Curie law for magnetism. It may be approximated for large values of x by the power series

$$L(x) \cdot = \cdot 1 - \frac{1}{x} + 2e^{-2x} + \ldots .$$

Here the polarization would not be proportional to F and it approaches a saturation value. This deviation from propor-

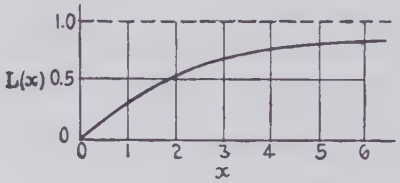

FIG. 59.

tionality occurs only for very high fields and in experiments especially designed to show this effect. In general, for small values of x one may write with sufficient accuracy

$$L(x) \cdot = \cdot \frac{x}{3} - \frac{x^3}{45} + \ldots .$$

Thus for the weak fields usually used $L(x) = x/3$, and hence

$$\frac{\overline{m}}{\mu} = \frac{1}{3}\frac{\mu F}{kT}$$

or

$$\overline{m} = \frac{1}{3}\frac{\mu^2 F}{kT}.$$

For electrons or charges which suffer displacement in an electrical field and thus produce a dielectric constant, the Clausius-Mosotti law gave

$$\overline{m} = \gamma F,$$

or

$$\gamma = \frac{\overline{m}}{F},$$

and where the quantity $\nu = 4\pi/3$ one had

$$P_0 = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho} = \frac{4\pi}{3} N_A \gamma.$$

If, however, permanent dipoles exist, they alone produce a quantity

$$\frac{\overline{m}}{F} = \frac{1}{3}\frac{\mu^2}{kT}$$

which must be their contribution to the measured polarizability of the molecule. Hence for molecules that have displaceable charges and constant dipoles the γ used before is not just the polarizability γ' due to displacement of charges but is given by

$$\gamma = \gamma' + \frac{1}{3}\frac{\mu^2}{kT}.$$

Thus, in general, the molecular polarizability P_0 should be written

$$P_0 = \frac{4\pi}{3}N_A\gamma = \frac{4\pi}{3}N_A\left\{\gamma' + \frac{\mu^2}{3kT}\right\} = \frac{\delta - 1}{\delta + 2}\frac{M}{\rho}.$$

Thus P_0 is a function of temperature and so is the measured $\frac{\delta - 1}{\delta + 2}\frac{M}{\rho}$ for all substances for which μ is not 0 (*i.e.*, all polar molecules).

It can be seen at once why $P_0 = \Omega$, the volume of the conducting spherical molecules is so abnormally great for NH_3, HCl, and similar gases. P_0 should be calculated from $\frac{4\pi}{3}N_A\gamma'$, which is the effect of the displacement induced by the field on the molecules considered conducting. But since μ is large for these molecules, the observed δ, which depends on both types of dielectric action, gives values for P_0 that are far too great, and hence values of Ω that do not agree with the real values. If γ' be estimated from the Van der Waals constants, then the relative importance of dipole and displacement effects can be estimated. Since the high value of μ is due to atomic grouping in certain molecules, it is a specific property of those molecules, and hence it is the appearance of a high μ in some groupings that interferes with the additive law. The Lorenz-Lorentz relation

$$\frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = P = \frac{4\pi}{3}N_A\gamma'$$

holds, shows little or no temperature variation, and shows additivity because for light the electrical fields alternate so rapidly that the molecules with their high inertias and low frequencies

of rotation cannot respond. Thus the contribution to γ by the permanent dipoles is nil and the value of P is governed only by the mobile displaceable electrons which can follow the field. Near a resonance frequency (*i.e.*, absorption band of the substance) the electrons are hampered in their motions, γ' is not given by the Lorenz-Lorentz law, and this theory fails. Thus one sees how simply and completely the qualitative discrepancies which lead to this investigation are explained. In the next section the quantitative agreement will be given.

97. Experimental Verification of the Debye Theory.—The new expression for the molecular polarizability P_0 is now

$$P_0 = \frac{4\pi}{3} N_A \left(\gamma' + \frac{\mu^2}{3kT} \right).$$

This takes on the form $P_0 T = a + bT$, where a has the value

$$a = \frac{4\pi}{3} N_A \frac{\mu^2}{3k},$$

and b the value

$$b = \frac{4\pi}{3} N_A \gamma'.$$

Thus $P_0 T = \frac{\delta - 1}{\delta + 2} \frac{M}{\rho} T$ plotted against T gives a straight line, whose intersection with the axis of ordinates evaluates a, and whose slope evaluates b. The results for NH_3 are plotted in Fig.

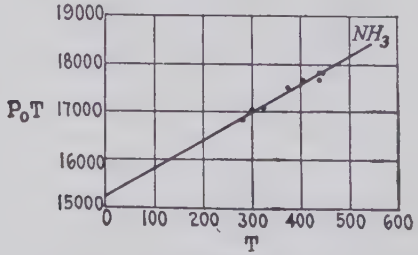

Fig. 60.

60. As is seen, they lie on a straight line within the limits of accuracy of the measurements. From these results a is found to be 15,250, and b 5.45. Since a has a finite value it must be assumed that NH_3 has a considerable permanent moment. Taking $N_A = 6.06 \times 10^{23}$ and $k = 1.37 \times 10^{-16}$, μ is found to be $\mu = 1.56 \times 10^{-18}$. If the electron is taken as 4.77×10^{-10}, the length of the dipole, that is, the distance between the charges is

3.27×10^{-9} cm, that is, assuming the dipole to be a single positive and negative charge separated by 3×10^{-9} cm one would obtain the value of μ observed. This distance is of the order of magnitude of the distances which atomic charges might be considered to assume between them in a molecule. The idea at once suggests itself that this distance might be equal to that between the nuclei of H and Cl in a gas like HCl. Zahn[11] has measured a and b for the three halogen acids, HCl, HBr, and HI. He obtains for μ divided by the electron the three values 0.217, 0.165, and 0.080×10^{-8} cm. That the value of μ/e should be less than the nuclear separation means merely that the interaction of the force fields of the charges in the molecule and their distribution give a dipole whose moment is equivalent to two elementary charges of opposite sign separated by a distance of 0.217×10^{-8} and 0.165×10^{-8} cm, that is, the two charges are not segregated in the centers of the two atoms. How the charges are distributed and how this is related to the nuclear distance is unknown.[13] It is sufficient for the theory that the value of μ/e is of the order of magnitude of 10^{-8} cm.

The value of b for NH_3 should give a reasonable agreement with the value of P calculated for optical frequencies (where the permanent dipoles do not figure) from the relation

$$P = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho}.$$

The agreement should not be perfect, owing to the presence of absorption bands. But extrapolation by means of the Cauchy formula to 0 frequency should yield values of P in rough agreement with b. P from such data comes out 6.13 cm^3, compared to the 5.45 observed for b above. This is a satisfactory agreement. From the relative magnitude of a/T and b one can get the relative magnitudes of γ' and $\mu^2/3kT$, the contributions of the displacement and dipoles to the polarization. Thus for NH_3, $a/T = 50.8$ and $b = 5.45$. Hence b is about one-tenth of a/T and the polarizability of the NH_3 molecules is due largely to its great permanent dipole moment.

These calculations hold unqualifiedly for gases. For liquids this is subject to a restriction. If the molecules with permanent dipoles are completely free to move and have their dipole strength unaltered in the liquid state by combinations, then the law must hold for both. If the liquid is one in which the molecules tend

to associate, that is, join in groups of two, three, or more molecules as the temperature changes, then the dipole strength is altered and the law does not apply. Both types of substances exist. Thus in ethyl ether some 50 values of P_0T from solid to gaseous state have been plotted in Fig. 61 as a function of T. From the critical temperature to the neighborhood of the melting point of the solid state T_s they lie on a straight line. Below the

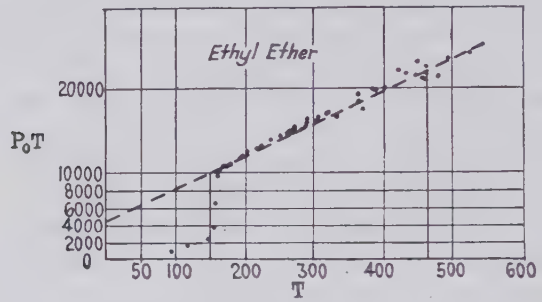

Fig. 61.

melting point they fall off rapidly. A similar change in dielectric constant for water is noted for the melting point. Thus water has a value of $\delta = 88$, while the value for ice is 3.8. This indicates an abrupt change of the dielectric constant on solidifying. The curve for ether gives $a = 4{,}400$ and $b = 38$. This gives a moment $\mu = 0.84 \times 10^{-18}$. The value of P from optical data is

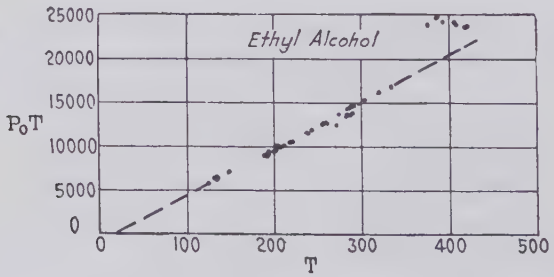

Fig. 62.

22.8 in rough agreement with b. The difference is due to the absorption in the infra-red. For ether $a/T = 14.7$ cm^3, which is less than one-half the value of b. Hence for this substance the displacement polarizability is more than double the permanent dipole contribution to the polarizability.

Figure 62 gives the curve between P_0T and T for ethyl alcohol, which is a typical associative substance. It is interesting to note

that again the points lie closely on a straight line. In this case the slope is such that a takes on a negative value. The five points above 350° lie on a different line. These were obtained from observations on the vapor. Could a straight line be drawn through them they would give positive values of a of considerable magnitude, indicating a high value of a/T and a relatively low value of b. Through association in the liquid state as temperature decreases the combinations of molecules annihilate the permanent dipoles. As these constitute most of the dipole strength, the rapid annihilation as association occurs gives the P_0T-T curve a slope in this region, which, if extrapolated to the axis of ordinates, would give a negative value. It is probable that the curve flattens out below 100° abs. and gives a positive

Formula	Name	Moment ($\times 10^{18}$)*
A	Argon	0
H_2	Hydrogen	0
O_2	Oxygen	0
Cl_2	Chlorine	(0.1)
Br_2	Bromine	0.45
I_2	Iodine	(1.2)
HCl	Hydrogen chloride	1.03
HBr	Hydrogen bromide	0.78
HI	Hydrogen iodide	0.38
H_2O	Water	1.85
H_2S	Hydrogen sulphide	0.95
NH_3	Ammonia	1.49
$SbCl_3$	Antimony trichloride	3.6
N_2O	Nitrous oxide	0
SO_2	Sulphur dioxide	1.61
CS_2	Carbon disulphide	0
COS	Carbonyl sulphide	0.65
CO_2	Carbon dioxide	0
CO	Carbon monoxide	0.11
CCl_4	Carbon tetrachloride	0
$CHCl_3$	Chloroform	1.05
CHN	Hydrocyanic acid	2.65
CH_3NO_2	Nitromethane	3.05
CH_4	Methane	0
CH_4O	Methyl alcohol	1.68
CH_5N	Methylamine	(1.3)
C_3H_6O	Acetone	2.80
$C_4H_{10}O$	Ether	1.12
$C_6H_5NO_2$	Nitrobenzene	3.90

* These are a few recent values taken from C. P. Smyth: "Polar Molecules."[14]

value for a corresponding to the solid state. Needless to say, measurements made in such liquids where association is taking place can lead to no values for a and b of any significance.

On page 497 is given a table of the dipole moments (*i.e.*, values of μ) for a number of substances:

The theoretical treatment of the question may be further extended to a study of the polarization in mixtures. Here again two classes of substances can be discerned—those mixtures in which no association takes place and those in which it occurs. The former are typified by ethyl ether-benzol mixtures. These follow the theoretical variation for the polarizability of the mixture which would be deduced from the percentage composition and the polarizability of the two molecular types. A study of the second type of mixture, such as benzol-ethyl alcohol mixtures, leads to very complicated curves. From an analysis of these curves Debye is able to segregate the part due to the polarizability of the alcohol and thus obtains a curve which gives the molecular polarization of the alcohol as a function of the concentration. This curve is given in Fig. 63. It is seen that this starts at 0 concentration with a value of 71.7 cm³ for P_0 and then increases. After passing through a maximum of 95 cm³ at 35 per cent it falls off to a value of about 50 at 100 per cent alcohol. The value at infinite dilution is the value for the unassociated single molecule. This is borne out by a measurement of the lowering of the freezing point, which indicates that at great dilutions the molecules are present as single units. Thus the measurement of the value of P_0 for alcohol can be made in dilute solutions. This has been done for other associative liquids also (*e.g.*, methyl alcohol, propyl alcohol, and nitrobenzol in benzol, and methyl alcohol in toluol). For ethyl alcohol the index-of-refraction method applied to the vapor gave a displacement polarization $P = 13.2$ cm³ and the liquid alcohol yielded 12.7 cm³. Taking the mean as 13 cm³, the contribution of the permanent dipoles in this to the total polarizability of 72 for the substance a/T is 59 cm³. Hence the moment μ for ethyl alcohol is $\mu \doteq 1.66 \times 10^{-18}$.

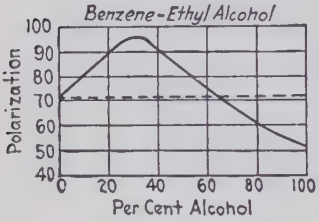

FIG. 63.

A further study of associative liquids could be made by a measurement and analysis of the molecular polarization of dilute solutions as a function of the temperature. These should yield a variation of P_0T with temperature of the form $a + bT$, and so lead to an evaluation of μ. This has been carried out by one of Debye's pupils. The explanation given by Debye of the form of the curve shown for ethyl alcohol in benzol is instructive. Owing to its high dipole strength, the alcohol molecules tend to join in groups of one, two, and more molecules. This tendency is counteracted by the temperature motion. In great dilutions they are, on the average, unassociated. At high concentrations the chance of association is increased, for, since they are, on the average, nearer together, groups form more often and more are in groups. It now remains to see how an associative substance can first increase its polarization and then decrease it as concentration increases. If two *spherical dipolar* molecules come together, their position of minimum potential energy is with the axes of the dipoles in line, the positive pole of one being near the negative pole of the other. The moment of such a configuration is twice the moment of a single dipole. For three such molecules the axes orient themselves in such a way that they lie along the sides of an equilateral triangle, each positive pole being towards the nearest negative pole. Such a configuration will have a resulting moment of zero. Thus the first stage of association has a moment double that of a single molecule, the second stage one which is zero. With this picture, if one add alcohol to pure benzol in increasing concentrations, at first one should get a formation of double molecules, that is, if this association were complete, one would have, instead of N_A molecules of moment μ and contributing to the molecular polarization a factor $N_A\mu^2$, $N_A/2$ molecules of moment 2μ which contribute to the molecular polarization a factor of $\frac{N_A}{2}4\mu^2$, that is, twice the original factor. Thus as long as the number of association groups of this type increases, the molecular polarization increases. As association progresses with increasing concentration, groups of the type of three molecules of zero moment will form. These contribute zero. As the number of these groups increases relatively to the bimolecular groups, the molecular polarization must drop rapidly. In practice, it is doubtful whether all groups take on the positions of minimum potential energy; but even approximation to this will

explain all the phenomena observed in this case. In nitrobenzol the polarization P_0 is 335 cm^3, while the value from the index of refraction $P = 33$ cm^3. This leads to a moment μ of value 3.90×10^{-18}. Such a molecule should show a marked association. This is the case for nitrobenzol, but in this case the molecular polarization does not increase at first as concentration increases, as was the case for alcohol. In fact, it decreases rapidly at first and more slowly later. The explanation of this would require a different model. Here the molecules would have to be ellipsoids of revolution with the minute dipoles parallel to the major axes at the center. In this case the molecules would associate by bringing the minor axes in contact and so have in the bimolecular state zero moment. It is obvious that such a picture is purely speculative, and it can be fruitful only in that it suggests further experiments.

Debye has also considered the case of electrical oscillations whose frequency lies between the infinitely slow oscillations giving P_0 and the rapid light vibrations giving P. In this region the time is long enough so that the alternating field changes sufficiently slowly to react on the permanent dipoles to an appreciable extent. Under these conditions the polarization will depend on the relation of the period of relaxation (*i.e.*, the time required for the molecular dipole to respond to the field) to the period of the alternating field. This must, in part, depend on the coefficient of viscosity of the surrounding liquid and on the size of the molecule. By an analysis using the law of equipartition and statistical relations similar to the treatment of Brownian motions, he arrives at a definition of the time of relaxation $\frac{1}{\omega_0} = \frac{8\eta a^3}{2kT}$, which is a characteristic of the particular substance, and determines its behavior. Assuming values for the constants for water, he computes that for values of $\omega_0 = 32 \times 10^{10}$ to 4×10^{10}, that is, for oscillations of wave length from 0.58 to 4.6 cm, water should begin to show the effect of its permanent dipoles in the value of P. The values of P are calculated on this basis, but the calculations are beyond the scope of this text. The values are complicated by absorption of energy in this region and their study properly belongs to the field of anomalous dispersion in light. According to Rubens the calculations are in agreement with experimental facts.

The calculation of the dielectric constant on the basis of the old quantum theory was first made by W. Pauli Jr.[12] and gave an equation which was in essence the same as the classical equation of Debye except for a numerical factor differing from the $\frac{1}{3}$ in the expression $\mu^2/3kT$. Later applications of the new quantum mechanics and the wave mechanics to simple polyatomic molecules have given equations which are, to first approximations, identical with the original Debye equation. From the application of wave mechanics to the molecules of diatomic gases, Debye[30] obtained an expression for the contribution of the permanent dipoles to the mean moment in the direction of the field F, which, to a second approximation, has the value

$$\bar{m} = \frac{\mu^2}{3kT}\left(1 - \frac{1}{3}\frac{T_k}{T}\right)F,$$

and for most cases approximates to within a few per cent the expression

$$\bar{m} = \frac{\mu^2}{3kT}F$$

in agreement with the classical value. In the second approximation $T_k = h^2/8\pi^2kI$, where I is the moment of inertia. Van Vleck[31] has derived an even more general equation valid for all types of gaseous molecules in which the $\frac{1}{3}\frac{T_k}{T}$ is replaced by a function $f(T)$ given by

$$f(T) = \frac{h^2}{48\pi^2kT\mu^2}\left[\mu_u^2\left(\frac{1}{B} + \frac{1}{C}\right) + \mu_v^2\left(\frac{1}{C} + \frac{1}{A}\right) + \mu_w^2\left(\frac{1}{A} + \frac{1}{B}\right)\right].$$

Here μ_u, μ_v, and μ_w are the components of μ along the axes u, v, and w; and A, B, and C are the moments of inertia of the molecule about the axes. Here again at ordinary temperatures the term $f(T)$ is practically negligible.

In his book Debye[30] goes to some length to show that the reason that the classical theory and the wave-mechanical theory differ so little is largely due to the fact that the polarization due to dipoles on the latter theory is the contribution of molecules with zero rotational energy so that temperature variation is caused by the loss or gain of these molecules. This point is brought out more clearly through a deduction of the classical equation in a manner more in conformity with the quantum

theory. These molecules with rotational energy in the higher quantum states do not influence the dielectric constant for the simple reason that through the influence of the field the contribution to the polarization for each quantum state of these molecules is as often positive as negative and thus yields zero total effect. This merely means that all molecules of sufficient energy, to have quantized rotations, are oriented parallel or antiparallel to the electrical field. Since these are equal in number for any quantum state, they contribute nothing to the dielectric constant and the latter depends on molecules with zero quanta of rotation.

If, however, molecules with dipole moments and quantized rotations are placed in an *inhomogeneous* electric field in a molecular beam, then those that set themselves parallel to the field are attracted and those antiparallel are repelled. The result is a splitting of the molecular beam into two portions when placed in an electrical field. Superposed on this splitting and displacement to each side of the position of the beam in the absence of a field is the attraction due to the *induced* dipole moments which are always attracted by the electrode since the dipole is induced by the field. Wrede,[32] later Estermann[33] in Stern's laboratory and still later McMillan[34] have succeeded in resolving molecular beams of polar molecules like HCl in an inhomogeneous electrical field in quantitative conformity with theory. On the other hand, non-polar molecules in such fields showed only the attraction due to the induced dipole moment. These experiments constitute the electrical analogue of the famous Stern-Gerlach experiment described in Sec. 101. The interpretation of the results is, however, more difficult, because the dipole moments are relatively small with the fields available and because the induced dipole moments are of the same order of magnitude as the permanent moments. In the magnetic case the diamagnetic action is so weak that it does not influence the paramagnetic behavior while there are molecules with no magnetic moments which enable the diamagnetic effects to be observed. It is unfortunate that lack of space makes it impossible further to discuss these beautiful experiments on electrical dipoles.

In conclusion to this discussion a brief word must be said of the significance and the value of the study of dipole moments in connection with molecular structure and kinetic theory. Since the first edition of this book was written, the study of molecular

polarization and of permanent dipole moments in relation to molecular structure has received a great deal of attention. The polarizability and the dipole moments of a great number of chemical substances have been determined such that, while in 1925 some thirty values were known, already in 1931 some thousand substances, organic and inorganic, had been studied.[14] The interpretations of these values in the light of molecular structure have been ably discussed in a recent monograph by C. P. Smyth[14] entitled "Dielectric Constant and Molecular Structure,"[c] and in Debye's "Polar Molecules."[b] The importance of such studies can be seen in the question of the arrangement of the molecule of water. Early structural formulæ for water as a result of purely chemical investigations appeared to indicate a linear molecule of the form H-O-H. Water, however, has a strong permanent dipole moment of 1.85×10^{-18}. This indicates that the two protons cannot be on opposite sides of the O molecule. A study of the moment of inertia of H_2O from its band spectrum, together with its dipole moment, fixes the molecule as a triangular arrangement of the mass points, the two protons lying on lines through the oxygen nucleus making an angle of some 64 deg., the protons lying inside the outer electron shell of the oxygen atom. Likewise NH_3 is shown to consist of the N atom at the summit of a tetrahedron with the three protons making the base. In this case the angle of the lines through the N atom and the protons make an angle of some 37 deg. with the normal from the N atom on to the plane of the protons. By combining the data from dipole moments and moments of inertia as determined from spectra with the data from the Kerr coefficients and depolarization in molecular scattering of light, H. A. Stuart[35] and his collaborators, assuming molecules in general to be ellipsoids of revolution, have been able to throw very valuable light on the molecular structure of more complicated molecules. Thus this field of investigation has yielded exceedingly valuable information both for chemistry and for the kinetic theory. Again in still another direction have the studies of dipole moments under the tutelage of Debye and others led to valuable information. This lies in the behavior of solutions of electrolytes and their dielectric constants. The behavior of the polar water molecules in the fields of the ions and dipoles of undissociated molecules in solution have enabled physical chemists to understand in at least a qualitative fashion

the complex phenomena observed as set forth by Debye in his fascinating book on "Polar Molecules."[b]

II. APPLICATION OF THE KINETIC THEORY TO THE MAGNETIC PROBLEM

98. Introduction.—In general, two types of magnetic action are recognized. These two types are exemplified by the classes of substances denoted as diamagnetic and paramagnetic substances, respectively. It is asserted, and generally believed, that the diamagnetic behavior is common to all substances, including the paramagnetic bodies, but that in the latter case the paramagnetic behavior where it exists is so much more powerful that it masks the diamagnetic behavior. The diamagnetic bodies can be characterized by two tendencies, both ascribable to the same action, that is, substances like Bi and Cu when placed in a strongly divergent magnetic field are repelled by the pole. Also when a rectangular piece or a piece of one of these metals having a greater length along one axis than another is suspended in a uniform magnetic field, the piece sets itself so that the long axis is at right angles to the magnetic field. These tendencies are real but on the whole relatively weak. The paramagnetic bodies, on the other hand, show just the opposite behavior, that is, they are attracted to the poles in a strongly divergent field and set themselves with their long axes parallel to a uniform magnetic field.

In terms of a picture of the magnetic field represented by Faraday lines of force, the diamagnetic behavior could be described by assuming that the diamagnetic bodies have *less* lines of force running through them than normally would exist in the space occupied by them, that is, they have a permeability less than unity which is ascribed to free space. For the paramagnetic behavior the tendency is to have a *greater* number of lines of force running through them than would pass through the empty space which they occupy, that is, they have a permeability greater than unity, the value for free space. For the *ferromagnetic* substances this increase in the lines of force is a very large number of times greater than unity, while for the diamagnetic case the reduction in permeability is not much below the value for free space. As will be seen later, the ferromagnetism is merely a type of behavior exhibited by paramagnetic bodies in the proper temperature

range. Paramagnetic phenomena have been ascribed to the existence in substances of small permanent molecular magnets, or molecular magnetic dipoles which can orient themselves in a magnetic field, so that their axes tend to correspond with the directions of the field, their north poles being oriented to the south pole of the field. Such an action would be counteracted by the disorienting heat motions of the molecules. Thus it would be expected that the permeability would decrease as temperature increased, and the paramagnetic properties would markedly depend on temperature. In this state they act as if the substance which they compose had become a magnet whose lines of force must be added to that of the inducing field, and, in fact, the quantities defining the effect of a field on a paramagnetic substance have, in part, been formulated from this viewpoint. To account for diamagnetism, it would be necessary, on a similar viewpoint, to assume that such a substance brought into a magnetic field had a magnetic field induced in the molecules present that opposed the existing field, and so reduced the number of lines of force passing through the body. That is, one would have to suppose that the atoms of Bi when brought into a field became magnets whose north poles were directed towards the north pole of the field.

An action of this type could at once be accounted for on the basis of Lenz's law of magnetic induction. If the molecules were of such a nature that they contained small *resistanceless* closed electric circuits, they would, when placed in a magnetic field, have currents induced in them, which, according to Lenz's law, would set up magnetic fields opposed to the acting magnetic field. Owing to the lack of resistance, these currents, and hence the field, would persist as long as the external field acted. In removing the external field, currents in the reverse sense and of equal magnitude would be set up, and when the field was gone there would be no resulting magnetism in the molecules or atoms. Such an action would manifestly be independent of temperature, for the disorientations of the molecules due to heat in the magnetic field would merely serve to annihilate the fields of some of the molecules while creating new field in others, since the orientation of the current circuits in the external field would be the determining action. This is found to be the case.

99. The Explanation of Diamagnetism.—The existence of such resistanceless circuits in the atoms and molecules seemed at first

an unreasonable hypothesis. The study of atomic structure in recent years has, however, definitely indicated that this must be the case. The existence of the electron, and the fact that it makes what might be considered an orbit about a central charged nucleus, must lead to just such an assumption. That the orbits in which the electrons move about the nucleus are relatively few in number, governed by certain energy and momentum relations, and that the radiation (*i.e.*, loss of energy) of the electrons in these orbits is zero are the fundamental assumptions of Bohr[15] which have led to the remarkable understanding of the atom in relation to spectra now obtaining. Thus an electron moving in a non-radiating (hence frictionless) orbit about the nucleus constitutes one of the hypothetical resistanceless electrical circuits.

Purely qualitatively, one may regard the effect of the introduction of such a molecule into the magnetic field in the following fashion. The electron moving in the orbit has a certain angular velocity, and hence possesses a mechanical moment of momentum. Consider such a mechanical system oriented in any fashion with regard to the field. It can then be regarded as a small gyroscope, the vector representing the moment of momentum being normal to the plane of the orbit. If, now, a magnetic field be produced, it will act on the electron so as to produce a mechanical force, for the electron in motion constitutes a current which is acted on by a magnetic field. Such an electron is pictured in Fig. 64, the nucleus being at N, the electron at E moving in its orbit. NO marks the vector representing the moment of momentum. In the particular case in question the force on the electron for all components of the motion perpendicular to the field and parallel to the plane of the orbit will be in a direction such as to exert a torque on the orbit, causing it to tend to rotate about an axis ANB normal to the field and in the plane of the orbit. For the components of the orbit normal to the plane of the orbit and normal to the field, the resultant forces will act so as to counterbalance each other and will produce no effect. On a rotating gyrostatic system the torque exerted on the plane of the orbit results in a precessional motion about an axis normal to the momentum vector NO and to the axis ANB about which the torque exists, that is, the gyrostat will undergo a precessional motion in the direction OP. Thus the electronic gyrostat will, as a whole, move so that the electron rotates in a plane which has a

component normal to the direction of the inducing field. But by Lenz's law the sense of this motion must always be such as to cause a field to be created in a direction opposed to the change in the flux through the circuit, so that, on putting on the field, the precession will be such that the magnetic field produced by

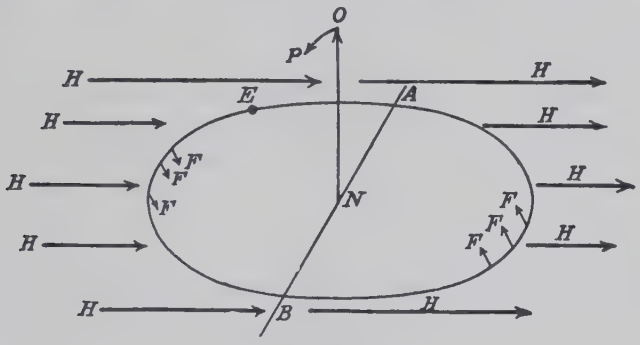

FIG. 64.

the electron of the orbit in its precessional motion will oppose the applied field, that is, the north pole of this precessional magnet will point towards the north pole of the inducing field. On removing the field, the precession will cease and the induced field will disappear. The torque on the electron, and the velocity of precession, and hence the strength of the induced or diamagnetic field, will be proportional to the inducing field. This will hold for all the i electrons in the atom or molecules.

Through analysis which properly does not belong in this text, it can be shown that the magnetic polarizability γ is given by an expression

$$\gamma = -\frac{e^2}{6m_1c^2}\sum \bar{r}_i^2,$$

where e is the electron, m_1 its mass, c the velocity of light, and r the average distance of the ith electron path from the nucleus. Now the mass susceptibility χ is given by $\chi = K/\rho$, where K is the magnetic volume susceptibility and ρ the density. For these considerations and those that follow the complicating correction for the inner magnetic field may be neglected, since the diamagnetic effects are so feeble as to make this unnecessary. But in analogy to the electrical case in Sec. 96, one may write P, the polarization for unit mass as given by $P = \rho zm$, where z is the number of molecules per gram mass, m is the moment induced

(which must be γH, where γ is the molecular polarizability, and H is the magnetic field strength). Thus, as

$$P = KH = \rho z m = \rho z \gamma H,$$

it follows that

$$K = \rho z \gamma \text{ and } \chi = z\gamma.$$

Hence

$$\chi = -\frac{ze^2}{6m_1c^2}\sum \bar{r}_i^2.$$

For a gram-atom χ_A, the mass susceptibility, will be

$$\chi_A = +A\chi = -\frac{N_A e^2}{6m_1c^2}\sum \bar{r}_i^2 = -2.85 \times 10^{10}\sum \bar{r}_i^2,$$

where A is the atomic weight and $Az = N_A$. Now $\sum \bar{r}_i^2$ is the sum of the squares of the average values of the displacements of all electrons from the nucleus, so that dividing $\sum \bar{r}_i^2$ by "Z," the effective nuclear charge,* one has a value for $\bar{r}^2$, the square of the average distance of the electron from the nucleus. A few values of $\sum \frac{\bar{r}_i^2}{"Z"}$ computed from χ_A are given in the table below. As is seen, the values are, on the whole, close to 10^{-16} cm^2, which is the order of magnitude of the square of the atomic radii, or, better, of the order of magnitude of the orbits of the electrons in the atoms deduced from the Bohr theory and spectroscopic data.

	Z	$-\chi_A$	$\sum \frac{\bar{r}_i^2}{Z}$
H	1	2.7×10^{-6}	0.95×10^{-16}
He	2	2.2×10^{-6}	0.39×10^{-16}
C	6	6.6×10^{-6}	0.38×10^{-16}
Cl	17	22.0×10^{-6}	0.45×10^{-16}
Br	35	33×10^{-6}	0.33×10^{-16}
Y	53	49×10^{-6}	0.32×10^{-16}
Hg	80	36×10^{-6}	0.16×10^{-16}
Bi	83	280×10^{-6}	1.2×10^{-16}

The explanation of the effect, by leading to an agreement of $\bar{r}_i^2$ as deduced from diamagnetic susceptibilities with the accepted

* The real nuclear charge Z is the electron multiplied by the number of the element in the periodic table. The effective nuclear charge is the real nuclear charge reduced by the screening action of other extra nuclear electrons than those considered.

values from other data, indicates the correctness of the explanation of the diamagnetic phenomenon.

The recent advances in the study of atomic structure which are summarized in Sec. 101 as it affects magnetic behavior enable one at this point to add one or two comments. In order to understand the terms used in these comments, reference to Sec. 101 will be required. The necessity of a whole section on atomic structure and quantization in order to understand the terms to be used makes it logical to place the comments at this point where they belong and refer those who are unfamiliar with this terminology to the complete discussion before reading these comments.

In a recent short but excellent monograph entitled "Magnetism," by Stoner,[e] detailed values of χ and of $\bar{r}^2$ are given, and the variation of these quantities with nuclear charge is shown, for the simpler electronic systems, to be a linear function as indicated above. In considering these data it must be pointed out that diamagnetic susceptibilities appear experimentally only in atoms having zero magnetic moment, *i.e.*, atoms having a resultant spin and orbital momentum of zero, or in general, atoms in the $^1S_0$ state. This condition applies especially to closed electron shells and thus occurs for the inert gases and the singly charged positive ions of the elements of group I and the single charged negative ions of group VII in the periodic table. It would also apply to doubly charged ions of group II in the periodic table and doubly negatively charged ions of group VI where they occur. The first values of $-\chi_A$ for the inert gases determined appeared to deviate from the values deduced from the ionized atoms of the same atomic numbers in solution. Later experiments of Wills and Hector[36] have, however, shown that the inert gases yield values in good agreement with the alkalies.

The quantum theory allows one at once to compute $\bar{r}^2$ on the theory of electron orbits. If the effective nuclear charge is "Z", $\bar{r}^2$ is given by

$$\bar{r}^2 = a_0{}^2 \frac{n^2}{\text{“}Z\text{”}^2}\left(\frac{5}{2}n^2 - \frac{3}{2}n_\phi{}^2\right).$$

Here $a_0 = 0.532 \times 10^{-8}$, the radius of the innermost orbit in H, *i.e.*, the unit Bohr orbit, while n is the principal quantum number and n_ϕ is the azimuthal quantum number. Thus the *orbit* n, n_ϕ will yield a value

$$\chi_A = -0.81 \times 10^{-6} \frac{n^2}{\text{“}Z\text{”}^2}\left(\frac{5}{2}n^2 - \frac{3}{2}n_\phi{}^2\right).$$

If one compute “Z” from the observed value of χ_A for He, assuming two electrons in the $n = 1$, $n_\phi = 1$ state, the value of “Z” = 0.93 whereas it should be about 1.7. For more complicated atoms the agreement between computed values of χ_A using spectroscopic data and the observed values is one of order of magnitude only. Van Vleck[37] and Pauling[38] have calculated χ_A on the new quantum mechanics and obtained an expression

$$\chi_A = -0.81 \times 10^{-6} \sum \frac{n^2}{\text{“}Z\text{”}^2}\left\{\frac{5}{2}n^2 - \frac{3l(l+1) - 1}{2}\right\},$$

where l is the orbital quantum number of the Sec. 101 and is $n_\phi - 1$ for a given orbit and Σ extends over all electron orbits in the atom. This equation gives the *effective* nuclear charge of He as 1.607 which is nearly the correct value. It should be noted that the “Z” used above is the effective nuclear charge. For one electron in an atom “Z” = 1. For more electrons in an atom the nuclear charge is partly “screened” off by the other electrons and so is reduced in value. Data from the ionization potential of He indicate that “Z” = 1.7 for neutral He in the ground state here considered. Pauling has attempted to calculate “Z” for a number of the inert gas atoms and gets a fair agreement. Hartree[39] has developed a “self-consistent field” method which enables the charge distribution fulfilling Schroedinger's wave-mechanical equation to be obtained more precisely. Stoner[40] applies this to calculate the diamagnetic susceptibilities with considerable success. If dN/dr is the charge in electron units per unit-radial distance from the atom, the total charge $\int_0^\infty (dN/dr)dr$ is equal to the number of electrons in the ion or atom. Hence,

$$\chi_A = -2.85 \times 10^{10} \int_0^\infty r^2 \frac{dN}{dr} dr.$$

The $r - \dfrac{dN}{dr}$ curves can be computed for a gas by means of wave mechanics and integrated. Applying this to He, Stoner obtained $\chi_A = -1.90 \times 10^{-6}$ in excellent agreement with observation. Other values of $-\chi_A \times 10^6$ follow in the table on page 511.

Substance	Calculated		Observed
	Stoner from Hartree field	Stoner from Slaters' "smoothed" wave functions	
He	1.9	1.6	1.9 ± 0.02
Ne	8.6	5.6	7.1 ± 0.5
A	24.8	18.4	19.2 ± 1.0
Na^+	5.6	4.1	5.4
K^+	17.3	14.2	13.4
Rb^+	29.5	25.3	23.0
Cl^-	39.6	25.3	24.0
Br^-	....	39.3	36.0

The values are in fair agreement. It is thus seen that in general the approach to the diamagnetic problem as outlined is satisfactory except that ignorance of many structural details and their effects has as yet not permitted a high degree of accuracy in calculation or theory.

Since the diamagnetic property is dependent on the electronic behavior on the inside of the atom, independence of temperature can be expected. Thus γ, and hence χ, should be found to be independent of temperature. Curie concluded that this was true from his experiments. Later experiments of Honda[16] and Owen[17] showed that this was not strictly true. The elements P, S, and Se show values of χ independent of temperature, while χ in Bi decreases as temperature increases, suffering a very abrupt change at the melting point. Again, it might seem as if the intrinsically atomic nature of the diamagnetic effect should lead to an additive value of γ for different atoms which combine to form molecules. Strange to say, this is, in general (with some exceptions), found to be true, for further reflection reveals that a complex molecule composed of several massive nuclei will not undergo the simple rotation as a whole on application of the magnetic field that one would expect in a single atom. For the following elements, then,

	χ_A
H	2.93×10^{-6}
C	6.00×10^{-6}
O	4.61×10^{-6}
Cl	20.1×10^{-6}

From this χ_A can be calculated for $H_2O = -10.5 \times 10^{-6}$, while the observed value is -12.9×10^{-6}. Again ethyl alcohol gives χ_A as -34.2×10^{-6} on computation, and the observed value is -30.5×10^{-6}. Since the orbits of outer electrons are changed by chemical combination, it is surprising that the additivity is as good as it seems to be. There are cases, such as in oxygen, where the atom in combination has its approximate diamagnetic susceptibility, while in some compounds, as in O_2, it is paramagnetic. On the other hand, it must be remembered that, besides the outermost valency electrons which are few in number, the orbits of most of the electrons are little affected by combination, so that χ_A could, on the whole, give a nearly constant average value in combination. The striking feature of this induced magnetism is that it fulfils much the same laws as does the induced dielectric polarization due to displaced electrons. The treatment of paramagnetism will show that this, in turn, acts analogously to the polarization produced in substances due to the existence of permanent dipoles.

100. Paramagnetic Phenomena in Their Relation to the Kinetic Theory.—As was stated in the introduction (Sec. 98), para- and ferromagnetism were early explained on the assumption of fixed molecular dipoles in the solids whose axes could be oriented by an imposed field. The diamagnetic action described in Sec. 99 must be present in all molecules, but must be completely masked, because of its small value, by the tremendous ferromagnetic effects. The term paramagnetism applies properly to all substances whose susceptibilities have a positive value, while the term ferromagnetic applies to a special type of paramagnetic action obtaining in some substances below a critical temperature. It is characterized by a very high susceptibility and an enormous inner field.

As far back as 1895 Curie,[18] who had been studying the magnetic behavior of substances, published a paper in which he concluded that for oxygen gas the paramagnetic susceptibility χ per unit mass was inversely proportional to the absolute temperature. Similar experiments on palladium and on ferromagnetic bodies that had lost their ferromagnetism at high temperatures confirmed him in his belief that these were to be explained on the basis of some common kinetic hypothesis. In the general phenomena of magnetism, Curie furthermore saw many analogies to the gas laws. In this he was supported by similar views

expressed as early as 1865–1868 by G. Wiedemann. The latter had found that the paramagnetic susceptibilities of solutions of different salts had a temperature coefficient of about the same value as that of an ideal gas. (He found this to be 0.0036 and Plessner later found 0.00355, while the true value for gases at this temperature is 0.00325.) This means, of course, the same thing that Curie found for oxygen, to wit that

$$\chi = \frac{C}{T},$$

where C is a constant and T the absolute temperature. Curie's work led Langevin[19] to derive the expression for the temperature susceptibility of gases on the basis of the kinetic theory. The treatment which he used is identical with the treatment given in Sec. 96 for the electrical polarization produced in a gas by the presence of permanent electrical dipoles, for Langevin assumed that the paramagnetic susceptibility was due to the existence of small permanent molecular magnets in each gas molecule. These were constantly being disoriented in a superposed field by the heat motions of the molecules. The only change to be made in the treatment for the magnetic case is that now the moment μ is the value of the moment of the permanent *magnetic* dipole in the molecule, the acting field is to be the *magnetic* field H instead of the electric field, and the average moment $\bar{m}$ is the average *magnetic* moment of the molecule. It follows at once that if, as the general distribution law demands the number of molecules having moments represented by vectors lying in a small volume element $d\Omega$ is given by $Ae^{\frac{\mu H}{kT}\cos\theta}d\Omega$, where θ is the angle of the dipole with the field, then the average moment for a large number of molecules may be written as

$$\bar{m} = \frac{\int_0^\pi e^{\frac{\mu H}{kT}\cos\theta}\,\mu\cos\theta\, d\Omega}{\int_0^\pi e^{\frac{\mu H}{kT}\cos\theta}\, d\Omega}. \quad \text{(See Sec. 96, Part I, Chap. X.)}$$

The solution of this yields

$$\frac{\bar{m}}{\mu} = \coth\frac{\mu H}{kT} - \frac{kT}{\mu H} = L\left(\frac{\mu H}{kT}\right),*$$

*Here $\coth\frac{\mu H}{kT}$ stands for the hyperbolic cotangent, $\frac{e^x + e^{-x}}{e^x - e^{-x}}$, where $x = \frac{\mu H}{kT}$.

where L stands for the Langevin function. Experimentally for paramagnetic substances, the fields H are always so weak that $\mu H/kT$ is small compared to unity. Thus the approximation given before can be used, namely,

$$L\left(\frac{\mu H}{kT}\right) = \frac{\mu H}{3kT} - \frac{1}{45}\left(\frac{\mu H}{kT}\right)^3 + \frac{\left(\frac{\mu H}{kT}\right)^5}{3{,}780} + \cdots$$

and therefore that, to a good degree of approximation,

$$\bar{m} = \frac{\mu^2 H}{3kT}.$$

For the sake of simplicity, in what follows it may be assumed that the inducing field H is the same as the inner field. This could not be done in the case of dielectrics, as, on the whole, the

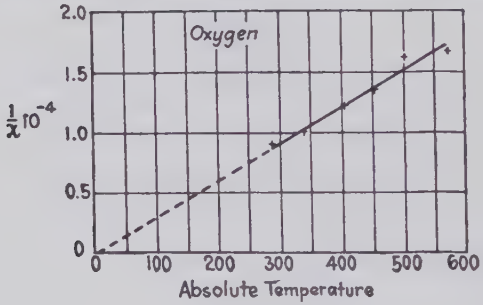

FIG. 65.

contribution of the other molecules to the field was considerable. As will be seen later, the magnetic polarization in paramagnetic substances is so feeble that the fields differ by less than 1 part in 1,000. One may, accordingly, write that as $KH = \rho z\bar{m}$, and $\chi = K/\rho$ (see Sec. 99), therefore

$$\chi = \frac{z}{H}\bar{m} = \frac{z\mu^2}{3kT},$$

where z is the number of molecules per gram. Thus $1/\chi$ is proportional to T. The extent to which this holds true can be seen in Fig. 65 for O_2 gas where $1/\chi$ plotted against T gives a straight line passing through the origin.

Instead of χ it is more convenient to use χ_M which is the value of χ per gram-molecule. Since, calling the atomic weight M, $zM = N_A$, the Avogadro number, $M\chi = \chi_M$, and one has

$$\chi_M = \frac{Mz\mu^2}{3kT} = \frac{N_A\mu^2}{3kT}.$$

Calling $\sigma_0^2 = N_A^2\mu^2$, one can write

$$\chi_M = \frac{N_A^2\mu^2}{3N_AkT} = \frac{\sigma_0^2}{3RT}.$$

Here σ_0 is the gram-molecular magnetic moment. Now Curie's law states that $\chi = C/T$, where C is the Curie constant per gram; accordingly

$$M\chi = \frac{MC}{T} = \chi_M = \frac{C_M}{T}.$$

where $C_M = \sigma_0^2/3R$ is the Curie constant per mole. Hence

$$\chi_M = \frac{N_A\mu^2}{3kT} = \frac{\sigma_0^2}{3RT} = \frac{C_M}{T},$$

and one identifies C_M with $\sigma_0^2/3R$. It is seen that this justifies the empirically discovered Curie law theoretically and evaluates the constants. It may be pointed out that the Curie law thus established is purely classical in that it allows of all values of orientation of the magnetic dipoles in the field. Actually, as is shown in the next section, the spatial quantization of magnetic moments in a magnetic field is an established phenomenon. Hence the proper derivation of the law must take into account the possibility of an effect due to the arrangement of dipoles in a few definitely oriented positions. The result will be to change the value of the factor $\frac{1}{3}$ which comes from an averaging over all directions in a continuous distribution.

It further follows from the observed deviation of a considerable number of solid paramagnetic bodies from the Curie law that a further modification of the theory is needed. Many bodies follow a law of the form $\chi = C/(T - \Theta)$, instead of the simple law $\chi = C/T$. Here Θ is a constant characteristic of the body which has the dimensions of a temperature, the critical temperature. This type of deviation was ascribed by Pierre Weiss to the neglect of the inner field produced by the effect of the fields of other dipoles on the one under consideration. In analogy to the inner field considered in the case of dielectrics, one must add to the external field H, imposed on the substance, the inner field $H_i = \nu I$. Here I is the intensity of magnetization per unit volume, and ν is the constant of the inner field which in the dielectric case was set at $4\pi/3$ for almost all dielectrics. Actually

in the case of a certain few dielectrics the value of ν may be a thousand times greater (see an article by Kobeko and Kurtschakow on the condition in the crystals of Rochelle salts[41]). A similar situation occurs in the case of the ferromagnetic substances which depart radically from Curie's law. In the case of magnetism the inner field may be very strong, and it is best to retain the factor ν instead of using $4\pi/3$ as for the dielectric case. Hence one can write that the effective magnetic field is $H_e = H + \nu I$. The nature of the circumstances leading to the high value of ν are not as yet clearly understood, although Heisenberg[42] has recently made an attempt of some value at its solution. The effect of H_e can be introduced into the equations for the case where $\mu H_e/kT$ is small, by replacing H in the expression

$$\bar{m} = \frac{\mu^2 H}{3kT}$$

by the value of H_e;

$$\frac{\bar{m}}{\mu} = \frac{\mu H_e}{3kT} = \frac{\mu(H + \nu I)}{3kT}.$$

For the average observed gram-molecular moment relative to the total possible moment per gram-molecule, one has

$$\frac{\bar{m}N_A}{\mu N_A} = \frac{\bar{m}N_A}{\sigma_0} = \frac{\sigma}{\sigma_0} = \frac{\mu N_A(H + \nu I)}{3N_A kT} = \frac{\sigma_0(H + \nu I)}{3RT},$$

where σ is the observed average moment per mole. If V_A is the molar volume, then $IV_A = \sigma$ and, since $M/V_A = \rho$, where M is the molecular weight and ρ is the density, one has $I = \rho\sigma/M$. Hence one may write

$$\frac{\sigma}{\sigma_0} = \frac{\sigma_0}{3RT}\left(H + \frac{\nu\rho\sigma}{M}\right).$$

Since furthermore $\chi_M = \sigma/H$, one has

$$\chi_M = \frac{{\sigma_0}^2}{3R\left(T - \frac{\nu\rho{\sigma_0}^2}{3RM}\right)} = \frac{{\sigma_0}^2}{3R(T - \Theta)},$$

where

$$\Theta = \frac{\nu\rho{\sigma_0}^2}{3RM} = \frac{\nu\rho}{M}C_M, \text{ and } C_M = \frac{{\sigma_0}^2}{3R}.$$

Thus $\chi_M = C_M/(T - \Theta)$, which is the Weiss law. It states that χ_M varies as $1/t$, where t is the temperature in degrees above a critical

temperature Θ, known as the Curie temperature, or Curie point. This constant Θ is positive and fairly high for ferromagnetic substances because of the high value of ν. At temperatures above Θ the effect of the inner field changes to smaller values, and one has paramagnetic phenomena. For paramagnetic substances Θ is small as ν is small, and for some substances Θ may be negative as well as positive. The equation can be rewritten in the form

$$\frac{1}{\chi_M} = \frac{T}{C_M} - \frac{\Theta}{C_M}$$

in which the reciprocal $1/\chi_M$ is proportional to T. This linear relation yields C_M from the observed χ_M by the slope, and Θ may be calculated from the intercept of the line with $1/\chi_M = 0$.

While above Θ ferromagnetism changes to paramagnetism, it does not follow that in the case of a positive Θ paramagnetism will give place to ferromagnetism if T is less than Θ. Ferromagnetism is a most peculiar and unusual state occurring only for the triad Fe, CO, and Ni in the periodic table and for the Heussler alloys of Mn, Cu, and Sn. It is seen at once that, from the temperature variation of χ_M, C_M can be evaluated, and thus σ_0 and μ, the magnetic moment of the atom, can be found. It was from such measurements of μ for a number of substances that Weiss evaluated his magnetic unit known as the Weiss magneton as the lowest common divisor of the observed moments. It has the value $M_W = 1{,}123.5$ unit moments per gram-molecule or $\mu_W = 1.85 \times 10^{-21}$ unit pole × cm. As is shown in the next section, there is no theoretical justification for this particular value, although it turns out to be closely one-fifth of the theoretical Bohr magneton μ_B. In fact, the data from which Weiss selected this unit were limited, and only one substance, Ni, showed a value as small as $3\mu_W$ while most substances have 10 or more Weiss units. While the Weiss theory leads to a form of the equation in agreement with observation, it is far from complete or perfect and the essence of its value of the inner field is unexplained. Furthermore, as before stated, even the Langevin theory must be modified to take account of space quantization so that further comparison with theory must be left until later. This space quantization did not apply to electrical dipole moments, as these are static and unless their rotation is quantized, these orient in all directions of space. In fact it is

the development of quantized rotation as temperature increases that is responsible for the temperature variation of the dielectric constant; for, as quantized rotations are taken up by the dipoles, these are oriented in the field in equal parallel and antiparallel positions giving zero total-moment. Magnetic moments are quantized in fields due to the moments of momentum associated with the orbits. In order to modify the theory, one may, following Stoner, proceed as follows.

Assume an atom of total quantum number J (see page 532) as a result of a total orbital quantum number L and a total spin moment S. The rules of spatial quantization state that the resolved moment M_r in the direction of the field can take on the following discrete values and no others, $J, J-1, J-2 \ldots -J$. The corresponding *magnetic* moment in Bohr units will be given by $M_r g\mu_B$, where $\mu_B g$ is the Landé splitting factor giving the ratio of magnetic to mechanical moment in an atom and g is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},$$

which is both theoretically derived from quantum theory and empirically established from the Zeeman effect. As was seen, the classical Langevin theory used the resolved magnetic moment $\mu \cos\theta$, which could have any value from $+\mu$ to $-\mu$. In the quantum theory the resolved moments are confined to the values given by $M_r g\mu_B$. In the deduction of the Langevin law, the average moment $\bar{m}$ in the field for an atomic moment μ was given by

$$\frac{\bar{m}}{\mu} = \frac{\int_0^\pi e^{\frac{\mu H}{kT}\cos\theta} \cos\theta \, (2\pi \sin\theta d\theta)}{\int_0^\pi e^{\frac{\mu H}{kT}\cos\theta} 2\pi \sin\theta d\theta}$$

where $2\pi \sin\theta d\theta = d\Omega$. For the case that $\mu H/kT$ is small, $e^{\mu H/kT} \cos\theta \cdot = .1 + \cos\theta$, so that $\bar{m}/\mu$ takes on the simpler form

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{kT} \frac{\int_0^\pi \cos^2\theta \sin\theta d\theta}{\int_0^\pi \sin\theta d\theta} = \frac{\mu H}{kT} \overline{\cos^2\theta}.$$

Here $\overline{\cos^2\theta}$ is the average value over all space. If the continuous distribution occurs, as it does for electrical dipoles, $\overline{\cos^2\theta} = \frac{1}{3}$, giving the approximation to $L(x)$, when x is small, obtained

before. In the case of space quantization the $\overline{\cos^2 \theta}$ must be replaced by $\overline{(M_r g/Jg)^2} = \overline{(M_r/J)^2}$. There are $2J + 1$ values of M_r extending from $+J$ to $-J$. Hence

$$\frac{\bar{m}}{\mu} = \frac{\mu H}{kT}\frac{1}{J^2}\frac{[J^2 + (J-1)^2 + (J-2)^2 + \ldots + (-J)^2]}{2J+1} = \frac{\mu H}{kT}\frac{(J+1)}{3J}.$$

Since Jg gives the total magnetic moment for an atom having a total momentum vector J, and as each unit Jg value represents a *Bohr* unit of magnetic moment, a Bohr magneton, $\mu_B = 3h/4\pi m$, then the quantity μ expressing the atomic magnetic moment can be written as $\mu = \mu_B Jg$. Thus

$$\bar{m} = H\frac{J(J+1)g^2\mu_B{}^2}{3kT}.$$

If $M_B = \mu_B N_A$ is the Bohr magneton per mole and N_A is the Avogadro number,

$$\chi_M = \frac{\bar{m}N_A}{H} = \frac{g^2 J(J+1)M_B{}^2}{3RT}.$$

To compare this with theory, recourse will most conveniently be had to the experimental moments evaluated in terms of Weiss magnetons. For a given substance the quantity $P = \sigma_0/1{,}123.5 = \sigma_0/M_W$ is usually determined. Here σ_0 is the observed gram-molecular magnetic moment evaluated by $\sigma_0 = \sqrt{3RC_M}$ from the Curie constant per mole C_M, and the $M_W = 1{,}123.5$ is the Weiss magneton per mole. Hence $P = \sqrt{3RC_M}/M_W$, and, if $1/\chi_M = T/C$, then $C_M = \chi_M T$ so that $P = \sqrt{3R\chi_M T}/M_W$. This can be placed into the quantum-theoretical equation for χ_M above, thus eliminating χ_M and evaluating P, since it turns out experimentally that $M_B/M_W = 5$ within the limits of experimental uncertainty.* Thus $P = (M_B/M_W)g\sqrt{J(J+1)} = 5g\sqrt{J(J+1)}$, where M_B is the Bohr magneton per mole. The simplest case on which to test the theory is an atom in the S state, *i.e.*, Na, K, Ag, etc. Here the magnetic moment is entirely due to spin, $L = 0$, $S = J$, and g is found to be 2. Hence $P = 5\sqrt{4S(S+1)}$. For 0, 1, 2, 3, etc., unbalanced

* Stoner in a recent letter to the author gives the value 4.952 for this factor based on Birge's estimate of the value of μ_B as 5564 ± 10.

electrons in the atoms, $S = 0, \frac{1}{2}, 1, \frac{3}{2}$, and the magnetic moments are 0, 1, 2, 3 Bohr units. The resulting table taken from Stoner[21] gives the magnetic moments of atoms in S states:

State	$^1S_0$	$^2S_{1/2}$	$^3S_1$	$^4S_{3/2}$	$^5S_2$	$^6S_{5/2}$
Bohr magnetons	0	1	2	3	4	5
P	0	8.6	14.1	19.3	24.4	29.4

These P values were first given by Sommerfeld, and they agree in order of magnitude with the P values observed for the ions of the first transition series. Since, in general, atoms and ions encountered are not in the simple S states, the more complete equation must generally be used. The equation was derived assuming that all the atoms of the substance were alike and in the same state of momentum, *i.e.*, that J was the same for each atom. If the temperature is high and the energy changes between different momentum states is small in comparison to

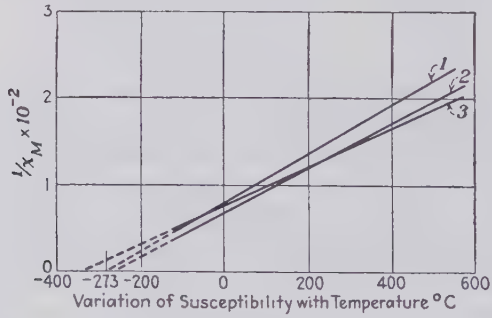

FIG. 66.

kT, the atoms will not all be in the same state, owing to the distribution of energies among the atoms. The problem has recently been rigorously developed on a quantum-mechanical basis by Van Vleck.[37] His equation shows that when the multiplet interval is large, the paramagnetic part of the magnetic moment is given by the equation just deduced. For the case that $\Delta\nu$ is the frequency difference between the different J states, then for $ch\Delta\nu \ll kT$, Van Vleck shows that the l's and s's are not strongly coupled and must be quantized separately with respect to the field. The previous equation must then be replaced by

$$P = 5\sqrt{4S(S+1) + L(L+1)}.$$

A comparison of theory and experiment is best given by Figs. 66 and 67. In Fig. 66 $-\frac{1}{\chi_M} \times 10^{-2}$ is plotted against temperature t in degrees C., for $FeSO_4$, $P = 26$, $\Theta = -16$, curve 1; for $MnCl_2$ $P = 27$, $\Theta = +21$, curve 2; for $Fe_2(SO_4)_3$ $P = 29$, $\Theta = -73$, curve 3. It is seen that the linear relation holds. In some cases abrupt changes in slope occur, due to changes in Θ, C, or chemical changes. For the same ion, in different salts, P has in general the same order of magnitude, but it may vary considerably, as for example, Chantillon[22] finds P

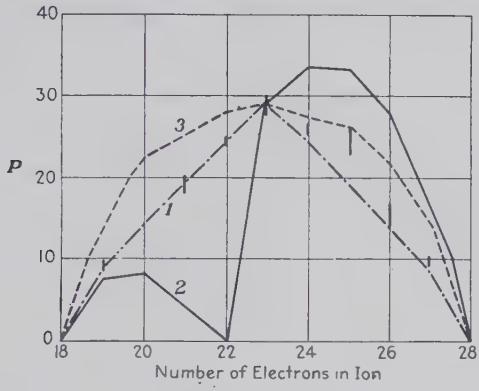

FIG. 67.

for the Co^{++} ion to lie between 22 and 26 in different salts. In Fig. 67 are plotted the calculated and observed magnetic moments of ions in the first transition series as a function of electron numbers as given by Stoner. The values of P are plotted as ordinates and electron numbers as abscissæ. The full curve indicates the calculated values of P given by $P = 5\sqrt{4S(S+1)}$, the dotted curve the values of P given by $P = 5g\sqrt{J(J+1)}$, while the dot-dashed curve gives the values given by $P = 5\sqrt{4S(S+1) + L(L+1)}$. The heavy vertical lines give the ranges of the observed values of the moments.

So far in the discussion nothing has been said of the portion of the domain where the fields are high enough to approach saturation. Thus, under ordinary conditions, $\mu H/kT$ is small so that the first approximation to the linear portion of the Langevin equation suffices. As T is lowered, the term can become sufficiently large so as to follow the Langevin law up toward saturation. This is the case for $Gd_2(SO_4)_3 \cdot 8H_2O$ with

the ion Gd^{+++} and 61 electrons. H. Kammerlingh-Onnes and H. R. Woltjer[20] made the measurements shown in Fig. 68. In this is plotted $\bar{m}/\mu$ against $\mu H/kT$ as a full curve from the Langevin equation, while the points are the observed values. The upper points correspond to an $\bar{m}/\mu$ of 84 per cent of the saturation value when at 1.31° abs. in a field of 22,000 gauss. The quantum theory, assuming an ion with a moment of seven Bohr magnetons, yields a saturation under these conditions of

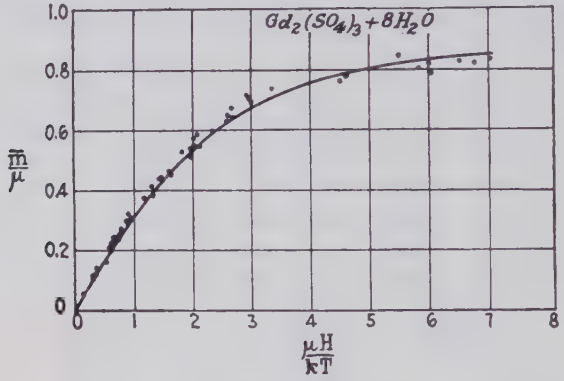

Fig. 68.

95 per cent. The confirmation of the theoretical Langevin equations in the case of $Gd_2(SO_4)_3 \cdot 8H_2O$, a solid substance, is quite surprising in view of the fact that the ions are rigidly fixed and are not free to rotate. It, however, may not be necessary to assume rotation of the rigid ion. The same result could be accounted for by assuming that the charge distributions associated with the ion in the field are such that the resolved magnetic moment can only have certain definite values. Taken as a whole, the results presented indicate again that the general considerations are correct and that, where the complex conditions encountered permit, the theory is in good agreement with fact.

101. A Summary of the Modern Picture of Atomic Structure in Relation to Atomic Magnetic Phenomena.—In the preceding sections the application of kinetic theory to the problem of dielectric and magnetic behavior in gases was given. This presentation was taken largely from the admirable treatise of P. Debye[8] in Marx's "Handbuch der Physik" which at the time of the writing of the first edition of this text in 1925, was one of the best and most modern treatments available. It had been

written largely from the classical mechanical point of view except to the extent that the old quantum theory was introduced wherever it applied. At the time Debye's original article was written, the general principles governing the application of the quantum rules were known as empirical principles. A great diversity of notation existed, and the real relation of spectroscopic and atomic magnetic data was not clear. The most troublesome factor, the half quantum numbers observed in so many phenomena, received their first explanation in papers by Uhlenbeck and Goudsmit[23] in 1925–1926 through the hypothesis that the electron might itself have a moment of momentum due to spin and with it a magnetic field. This suggestion led to a rapid clarification and unification of the whole problem of atomic physics, too late for inclusion in that text. The development of the new wave mechanics in the period 1925 to 1927 aided materially in the understanding of relations throughout the domain of atomic physics. Thus, already by 1928, Dirac[24] had shown that the spin moment was a natural consequence of the appropriate relativistic generalization of the quantum-mechanical equations for the electron. Consequently in writing the second edition of this book it becomes essential to include the results of the recent investigations on magnetic phenomena at the appropriate sections in the text. In order that these results may be understood, it was considered important to add this section furnishing the key to the terminology there used to replace the sections on ferromagnetism in the old text which do not properly belong here. In this section, however, too detailed a discussion of the problem is not possible, owing to the fact that the problem is essentially one of atomic structure and wave mechanics and a more complete treatment would require the laying of an elaborate foundation of considerable length, to say nothing of the development of the problem which of itself could easily fill a book.

The problem can be taken up with the criterion set forth by Bohr[25,f,43] in 1913 to define the stable orbits in a nuclear atom. This criterion was the quantum restriction which stated that in an atom the moment of momentum of the electron in a stable circular orbit must be governed by the relation $p = nh/2\pi$, where n was a whole number. In addition, an electronic orbit must be governed by the condition that the centripetal Coulomb force Ze^2/r^2 on the electron of charge e by a nucleus of charge Ze

(Z being the atomic number) in an orbit of radius r must equal the centrifugal force mv^2/r, whence $mv^2 = Ze^2/r$. Since p in this case is $mvr = nh/2\pi$, one can at once write that, for stable orbits, $r = n^2h^2/4\pi^2Ze^2m$ and $v = 2\pi Ze^2/nh$. This fixes the properties of the orbit once Z and n are fixed. As n increases, the radius of the orbit increases, and hence for $n = 1$ one has the innermost orbit for a given value of Z. For $Z = 1$, $n = 1$, one has the innermost orbit for the simplest of the atoms, the hydrogen atom. This orbit was considered by Bohr to be the *unit orbit*, and many orbital properties are referred to it as the unit. It furthermore appears that when one considers two orbits in which the energy is E_a and E_b corresponding to values of $n = a$ and $n = b$, $b > a$, one has the frequency ν_{b-a} radiated in a transition from the outer orbit $n = b$ to the inner orbit $n = a$, given by

$$\nu_{b-a} = \frac{2\pi^2mZ^2e^4}{h^3}\left(\frac{1}{n_a{}^2} - \frac{1}{n_b{}^2}\right).$$

It is seen at once that the quantity n fixes the properties of the orbit, its radius r, the orbital velocity, the energy of the electron, and, in a given transition of an electron from one orbit to another, it determines the frequency of light radiated or absorbed. It is seen that this important number which from now on will be termed the *principal quantum number* and will be designated by the symbol n is of prime importance in describing the electronic state in the atom. As will later be seen, there are in general several differently shaped orbits possible for all values of n beyond $n = 1$, but these strangely do not affect the influence of n as regards the energy in the orbit. It will also later transpire that, as an atom is built up by adding electrons about a nucleus, there will be a limit to the numbers of electrons which can go into orbit types with the same value of n. As lower n values are occupied with electrons, then only higher values of n can be filled, and each increase in n means a larger r. Thus, owing to the values of r as determined by n, the electrons will be grouped in several shells or levels in the atom with widely diverse energies. Thus n is responsible for a stratification of electrons into levels in the atom. These levels have been identified with those regions of the atom which emit the various characteristic X-rays. Thus as n takes on values 1, 2, 3, 4, etc., the values of n in the atom are identified with the K, L, M, N, etc., X-ray levels in the atom.

Having now described the nature of the influence of n on the atom, one may consider the case of the orbit for which $n = 1$. In this case, as will later be seen, the orbit is a circular orbit and in addition, if $Z = 1$, one has the simplest orbit imaginable.

This simple orbit of hydrogen, $Z = 1$, with $n = 1$, $mvr = p = h/2\pi$ (see Sec. 100), Bohr chose as his orbit of unit of moment of momentum, as stated before. In such an orbit there is created a *magnetic* moment μ due to the revolution of the electron about the nucleus. This moment can at once be calculated from the well-known law that a current i about an area A gives a magnetic shell of moment μ, thus $\mu = iA$. Since $i = e/T$, where e is the charge and T is the period of revolution, $\mu = eA/T$; and as $\frac{p}{2m} = \frac{A}{T}$, then, since in general $p = \frac{nh}{2\pi}$, $\mu = \frac{ep}{2m} = \frac{nhe}{4\pi m}$. In all that follows it must be remembered that e is in electromagnetic units; if e is expressed in electrostatic units, e/c must be used. The quantity μ is the magnetic moment associated with the nth orbit and for the unit Bohr orbit, for which $n = 1$, $\mu = he/4\pi m$, which *should be the unit magnetic moment.* Hence it might be expected that the properties of this simplest of orbits would appear as a sort of fundamental unit in studies of the magnetic properties of atoms.

Actually the conditions in the atom are not so simple as outlined above, for the orbits in general will not be circular. Central forces with closed orbits in general demand elliptic orbits of which the circle is just a special case. In the analysis of the quantization of an elliptical orbit it transpires that polar coordinates are the convenient coordinates to use, and the motion is quantized along the radius vector and about the origin in azimuth. Thus the conditions imposed in quantization (see Sec. 92*a*) are that

$$\int_{\phi=0}^{\phi=2\pi} p_\phi d\phi = n_\phi h, \text{ and } \int_{\phi=0}^{\phi=2\pi} p_r dr = n_r h.$$

Here p_ϕ and p_r are the momenta for the azimuthal coordinate and the radial coordinate, while n_ϕ and n_r are integers expressing the azimuthal and radial quantum numbers. An evaluation of these quantities in terms of the analytical geometry of the elliptical orbit shows that the equation for the frequency of the light emitted in a transition from one elliptical outer orbit k to an inner elliptical orbit n is given by

$$\nu_{k-n} = \frac{2\pi^2 me^4 Z^2}{h^3}\left[\frac{1}{(n_\phi + n_r)^2} - \frac{1}{(k_\phi + k_r)^2}\right]$$

instead of

$$\nu_{b-a} = \frac{2\pi^2 me^4 Z^2}{h^3}\left(\frac{1}{n_a{}^2} - \frac{1}{n_b{}^2}\right)$$

as for the circular orbit. This indicates that the introduction of ellipses does not change in any way the energy criteria laid down for circular orbits, for it is seen that for any values of n_a and n_b the elliptical orbits alter the situation only by replacing the single integral quantum numbers n_a and n_b each by the sum of two integral quantum numbers, $n_\phi + n_r = n_a$ and $k_\phi + k_r = n_b$. Thus the *frequency* radiated is the same as long as $n_\phi + n_r = n_a$ and $k_\phi + k_r = n_b$, irrespective of the shape of the ellipse, which will vary as the azimuthal quantum number n_ϕ is greater than, equal to, or less than the radial n_r. As stated before, n_a and n_b are thus called the principal quantum numbers which determine the size of the orbit and hence the energy in the orbit. Since n_ϕ and n_r are integers, it is seen that the number of differently shaped ellipses is quite limited for small values of n_a or n_b, the principal quantum numbers. It turns out that the orbit for which $n_r = 0$ is the circular orbit, for the radius vector is then constant and there is no change in r. The elliptical orbit with $n_\phi = 0$ is degenerate and is excluded; for in this case the electron would oscillate in a straight-line path through the nucleus which it cannot do. Orbits of decreasing n_ϕ and increasing n_r for a given principal quantum number are increasingly elliptical, the most elliptical being the orbit for $n_\phi = 1$ and $n_r = n - 1$. Since n_ϕ cannot be less than 1, and since n_r can equal 0, the number of possible orbits is fixed by the value of n to give *just n possible orbits*. For convenience and in conformity with usage in wave-mechanical analysis, n_ϕ, in the study of atomic problems, is replaced by a symbol $l = n_\phi - 1$, which takes on integral values beginning at zero for $n_\phi = 1$. Thus, while $n_\phi = 1, 2, 3, 4$, etc., $l = 0, 1, 2, 3, 4, \ldots$, when $n_r = \ldots 3, 2, 1, 0$. Hence the condition of the orbit is defined by n and l, n having integral values beginning with 1, and l taking values successively 0, 1, 2, 3, etc., the orbits being more and more elliptical, the smaller l. In relation to spectroscopy, electrons in these orbits $l = 0, 1, 2, 3$, etc., are said to be of the s, p, d, f, g types, respectively, corresponding to the nomenclature, sharp, principal, diffuse, etc., of the series

of lines with which they are associated. Thus it is seen that, in one plane, n defines the area of the orbit, and the energy associated with it, while a number l of which for each n there are n values 0, 1, 2, 3, . . . n, defines the shape of the orbit and hence, as will be seen, the moment of momentum.

In the discussion of the possible motions of the electrons about the nucleus, only the motions of the electron in one plane have been so far discussed. Actually the plane of the electron orbit may also be oriented in space. In the case of a single electronic orbit, however, as long as no direction in space about the nucleus is specified, *i.e.*, by the introduction of some vector quantity into the picture, such as an external electrical or magnetic field, or the presence of some other electron orbit, one need not concern oneself with spatial orientation. When, however, the atom finds itself in a magnetic or electrical field, or one must consider the relations between two or more orbits in an atom, the question of spatial orientation and quantization must be considered. In the present consideration of the quantization in space, conditions must, for simplicity, be so chosen that the fields fixing the direction in space are so small as not to alter the energies in the orbits appreciably. The motion of the electron can then be described in three-dimensional polar coordinates in terms of two angles θ and ψ and the motion along the radius vector. The separate quantization discussed in Sec. 92*a* requires that the conditions

$$\int p_\theta d\theta = n_\theta h,$$
$$\int p_\psi d\psi = n_\psi h,$$
$$\int p_r dr = n_r h$$

be fulfilled, wherein n_θ, n_ψ, and n_r are the integral quantum numbers along the three polar coordinates θ, ψ, and r. The process of quantization yields a most interesting result. Again the energy values as given by the principal quantum numbers n are unaffected, and the radial quantum number n_r is also unchanged. However, n_ϕ for the plane orbit, under space quantization is found to be the sum of two integers, the *angular* quantum numbers n_θ and n_ψ. Thus space quantization yields the fact that $n_\phi = n_\theta + n_\psi$ and $n = n_r + n_\phi = n_r + n_\theta + n_\psi$. A still more important relation is revealed by this spatial quantization which is as follows. If α is the angle between the moment

of momentum in the orbit and the chosen direction in space set either by some magnetic or electric field, it turns out that

$$\frac{p_\psi}{p} = \frac{n_\psi}{n_\phi} = \frac{n_\psi}{(n_\psi + n_\theta)} = \cos \alpha.$$

This signifies that, since n_ψ and n_ϕ are integral numbers, the *component* moment of momentum, p_ψ, of an electron in an orbit having a moment of momentum p, projected on the equatorial plane about the chosen field direction, is also quantized; for p is integral as is the ratio $n_\psi/n_\phi = p_\psi/p$. Hence p_ψ, the component of the momentum of the orbit p resolved along the lines of force, is a whole numbered multiple of $h/2\pi$. It is seen at once that this places a restriction on the value of the angle α between moment of momentum p and field direction. For cos α is limited to only a few discrete values defined by p_ψ/p. In discussing this question it must be borne in mind that the moment of momentum is a vector quantity whose direction lies normal to the plane of the orbit and whose magnitude depends on the orbit. It is thus seen that the magnetic moment of the electronic orbit, in view of the revolution of the electron, is parallel to the vector representing the electron's moment of orbital momentum, and that the quantization of the momentum and restriction of the orientation of this moment in the field to a few discrete values of α also limits the positions which the magnetic axis of the orbit can take in a space where a field exists. Such quantized behavior of the magnetic moments in electron orbits, it is seen, must profoundly influence the magnetic behavior of atoms. It is also seen that through such action the restriction of the orientation of the electron orbits in magnetic or electric fields to certain specified directions must influence in a definite fashion the effect of such fields on the light emission in these fields. Thus it is to be expected that much information will be gained concerning such phenomena as Zeeman and Stark effects by the analysis above. Since cos $\alpha = n_\psi/n_\phi$, it is seen that for small values of n, and hence n_ϕ, cos α will take on a very few definite values. It was stated that at times it was convenient to replace $n_\phi - 1$ by the symbol l. In what will follow the quantity n_ϕ in *space* quantization will be replaced by the symbol j. This quantity j is *not just* n_ϕ as it will be found to include a new term to be discussed presently. It will, however, represent the *total moment of momentum of the electron orbit which orients*

itself in the field and will contain more than n_ϕ. For the present it will be treated as synonymous with n_ϕ. The effect of space quantization can be seen in the few simple examples which follow. As a result of the foregoing, one finds that for the case where $j = 1$, $\cos \alpha$ ($\alpha = \pi/2, 0, \pi$) can be 0 or ± 1, for n_ψ can be 0 or ± 1. For $j = 2$, $\cos \alpha(\alpha = \pi/2, \pm 60°, 0, \pi)$ can have the values 0, $\pm \frac{1}{2}$, ± 1, as n_ψ can take values 0, ± 1, ± 2, etc.

From these rules resulting from quantization, one can survey the possible orbits open to electrons about a nucleus. In the first place the radial parameter of the orbit and hence its energy are governed by n, the principal quantum number, which can be 1, 2, 3, 4, etc., and together with Z, the nuclear charge, fixes the magnitude of the radius of the equivalent circular orbits. Again n_ϕ, or $l + 1$, fixes the *shape* of the orbit for a given value of $n = n_\phi + n_r$. This gives for each value of n, n differently shaped ellipses beginning with $n_r = 0$ for the circular orbit. In addition, with a fixed direction in space defined by some field, the axis of each of these orbits is restricted to angles α with the field which amount to $4j$ in number for each of the ellipses representative of that value of j.

These relatively simple relationships as to the kinds of electron orbits made it appear possible to predict the electron arrangement in the atoms and hence also to predict the nature of the spectra emitted by atoms in both the presence and absence of fields.

In the meantime, beginning with the work of Catalan in 1922 and that of Russel and Saunders,[26] a certain amount of order was being introduced into the relation of spectra to the atomic concepts just discussed. It had already far earlier been possible to identify the principal quantum numbers with the series of X-ray levels in the atoms so that $n = 1$ was associated with the K series, $n = 2$ with the L series, $n = 3$ with the M series, etc. Furthermore, the studies of Zeeman and Stark effect spectra indicated that there were close analogies between the orbital quantizations derived from theory and those observed. Difficulties were, however, encountered in obtaining numerical agreements, especially as the spatial quantization terms appeared to indicate the necessity of the use of half quantum numbers in the j values. Bohr's studies of these questions made the use of such terms seem imperative.

In the meantime another series of investigations concerning the existence of the orbital electrons in atoms through a study

of the magnetic behavior had thrown some interesting light on the same problem. S. J. Barnett[27] had argued that if, as postulated in Sec. 99, the electrons in their orbits actually represent miniature gyroscopes, a mechanical torque on these orbits produced by spinning a bar of metal should also produce a precession of the orbits just as does the imposed field in diamagnetism. Thus if an unmagnetized bar be spun at high speed in the absence of a magnetic field, the torques on the electron orbits should produce a precession such as to give an axial magnetic field. Using ferromagnetic rods, carefully demagnetized, in order to increase the feeble effects due to the weak mechanical forces by the induction in the iron, Barnett, after overcoming great difficulties, obtained a measurement of the effect which was in the correct direction and of the right order of magnitude. There was, however, a discrepancy between theory and the later accurate results obtained, which in magnitude was closely a factor of 2. Independently and somewhat later, Einstein and de Haas[45] succeeded in producing the inverse effect, namely, a mechanical oscillation of a rod subjected to an alternating field as a result of the reaction to the magnetically produced precessions. Again the values of e/m for electrons to be inferred from these experiments on classical theory were off by a factor of 2. There was thus clearly some theoretical difficulty inherent in the assumptions of the classical theory, which could not be located with ease but again involved a factor of 2. As a result, however, of the excellent spectroscopic data and the theoretical investigations of Pauli, Goudsmit, Heisenberg, Hund, and, finally, of Uhlenbeck and Goudsmit,[46] a scheme of analysis according to purely empirical rules was worked out, which is known as the vector model. While empirical, the success of the analysis was quite striking. The essential missing element in the vector model was supplied in an hypothesis of Goudsmit and Uhlenbeck[23] that the electron *itself* had an intrinsic spin moment equal to $\frac{1}{2}(h/2\pi)$ or $\frac{1}{2}$ of the Bohr unit of moment of momentum in the orbit for $n = 1$ and a magnetic moment equal to $\frac{e}{2m}\frac{h}{2\pi}$ which is just the magnetic moment of an electron in the simple Bohr orbit for which $n = 1$. Dirac[24] subsequently showed that this hypothesis was justified. Thus the electron is associated with a spin moment or vector designated by the symbol s.

Thus, besides the quantization of l, the azimuthal quantum number in space due to a field, there must be included in the quantum number j, representing the quantum number of the orbit as a *whole*, the spin moment s of the electron itself. Since it was stated above that $s = \frac{1}{2}$ a Bohr unit, and as the spin moment can be opposed to or in the same sense as the orbital moment, s can take on only values of $\pm\frac{1}{2}$ Bohr unit of momentum. Thus the total angular momentum quantum number of an electron orbit, which is the vector sum of l and s, is called j, such that $j = l \pm s$, and j can take on only half integral values. This at once explains why the spatial quantization rules for single electron orbits when measured did not give the orientations to be expected before the spin moment was included. Such a result follows because the combinations of directions which give projections on the field axis differing by integral values yield different angles α when the vectors to be quantized are half integers than when they are whole integers. Thus, for instance, for $j = \frac{1}{2}$, with $l = 1$, $s = -\frac{1}{2}$, the projections on the field axis are ± 1 but not 0. Hence an orbit for $l = 1$, $j = \frac{1}{2}$ can only set itself with its normal parallel or antiparallel to the field. For $l = 1$, $s = +\frac{1}{2}$, $j = \frac{3}{2}$, the orbit can set itself so that its normal is parallel or antiparallel to the field, or such that it makes an angle for which $\cos \alpha$ is $\pm\frac{1}{3}$. It is thus seen why for single orbits j values are used in quantization instead of the l values alone. In the presence of large magnetic fields, the orientations of these orbits take place so that the projections of the l's are integers and of the s's are half integers, respectively. These projections on the field are called the magnetic quantum numbers and they are designated by the symbols m_l and m_s. Here m_l is defined by integers lying between the limits $-l \leq m_l \leq l$, and m_s is defined by half integers lying between the limits $-s \leq m_s \leq s$. Thus m_l may have $2l + 1$ values from $-l$ to $+l$, and m_s has values $\pm\frac{1}{2}$. Hence for a given value of l one has a total of $2(2l + 1)$ possible orientations of the orbits.

If one proceeds to consolidate the several electron orbits into the atom to analyze its behavior as a whole, one must take into account the mechanism of interaction of the electrons in the atom, termed the coupling. This coupling determines the spectrum terms of the energy levels. If the separate l's and s's of the individual electrons exert the principal influence, it may be assumed that the separate vectors corresponding to these

terms add vectorially to give the L and S vectors of the atom as a whole. Thus one can write $L = \sum_i {}_v l_i$ and $S = \sum_i {}_v s_i$, where l_i is the value of l for any one of the i electrons and s_i is the value of s on any one of the i electrons. Hence the orientation of the l's gives a series of L values which correspond to the characteristics of spectroscopic term series S, P, D, which appear in the Grotrian diagram (reference *f*, page 229) for term series of the atom. The vector sum of L and S gives J, the total angular momentum vector of the atom. This is also quantized. It has half-integral values if S is a half integer and integral values of S if an integer. The J value appears as a subscript to the letter indicating the L value. This type of coupling is called the Russel-Saunders or L-S coupling. Other types are possible, of which the extreme case is one in which the l and s vectors of each electron give the j values whose sum is the atomic J value.

The rules for quantization together with the exclusion principle of Pauli at once enable one to indicate the structure of any atom. The exclusion principle says that for no two electrons in an atom may the four quantum numbers of any particular electron, the ith, be the same. That is, no two electrons can in the same atom at the same time have the same values n_i, the total quantum number; l_i, the orbital quantum number; m_{li}, the component of l_i along the field; and m_{si}, the component of s_i along the field. This obvious rule merely says that *one and only one electron in an atom at one time can be in a given state defined by the four quantum numbers.*

This rule leads at once to the orbit sequence in which electrons must enter an atom of atomic number Z as each electron is added, provided one assume that the electrons prefer to go to states of the lowest quantum number possible. It is clear then that the Z electrons required to complete the electronic quota of the atom will each seek orbits so differing in the number n_i, l_i, m_{li}, and m_{si} as to attain the lowest quantum states, each electron, however, keeping its individual state free for itself. Thus the number and type of orbits for Z electrons can at once be chosen and a fairly good picture of the atom can be obtained.

For example, the first electron goes into an orbit for which $n = 1$. Thus its l and m_l values are 0, and its m_s value can be $\pm\frac{1}{2}$. If it takes the value of $m_s = +\frac{1}{2}$, another electron can

enter the atom with $n = 1$ and $m_s = -\frac{1}{2}$. The $n = 1$ orbit is then filled, and this grouping of electrons completes the $n = 1$ or K shell or level in the atom. All atoms of whatever Z must have this group, for the first two electrons added will take this low-energy state. If a third electron is added, it cannot go to an $n = 1$ orbit. Thus, for the next electron, n must be 2. Here one has the beginning of the L electron shell or level. For $n = 2$, $l = 0$ or $l = 1$. If $l = 0$, there is no moment m_l, and m_s can have values $\pm\frac{1}{2}$. Thus the next two electrons go in to form a group with $n = 2$, $l = 0$, $m_l = 0$, and $m_s = \pm\frac{1}{2}$. If it went into the $l = 1$ orbit, then it could take values of $m_l = -1$, 0, $+1$, or $2l + 1$ possible orbits and for each value of m_l, m_s can be $\pm\frac{1}{2}$. There are thus six possible orbits that can be filled and six more electrons can be added, corresponding to the $2(2l + 1)$ combinations. Whether the electrons first go to an $l = 0$ in preference to an $l = 1$ grouping cannot be predicted, but spectral and chemical data show that in general the electrons will go into the $l = 0$ group first and later into the $l = 1$ groupings. After this with two $n = 1$ electrons in the K shell and $8 = 2 + 6$ electrons in $n = 2$, the $n = 2$ or L shell is full and subsequent electrons must go to the $n = 3$ or M shell in the atom. Under these conditions the shell is said to be closed and a new shell begins.

Since for each value of l there are $2(2l + 1)$ possible orbits, one can calculate the number of electrons in the closed shells corresponding to $n = 1, 2, 3, 4$. This is seen in the following table.

n	Type-s orbit	Type-p orbit	Type-d orbit	Type-f orbit	Total orbits
1	2	..	..	..	2
2	2	6	..	..	8
3	2	6	10	..	18
4	2	6	10	14	32

The closed shells have a very important property judged from the point of view of the moments. Consider the 10 type-d electrons for which

$m_l =$	2	2	1	1	0	0	-1	-1	-2	-2
$m_s =$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

It is seen that this shell has the resultant L, S, and therefore J, equal to zero. The same holds for all of the closed shells. Accordingly the effect of a closed group may be neglected in calculating the atomic moment. Thus the types of orbits giving moments and affecting orientations in fields are those which exist outside of the closed shells. The fact that these closed shells occur for groupings of 2, 8, 10, etc., electrons enables one to explain certain regularities of the periodic table. As Z increases step by step, more electrons must be added to make the atom neutral. Hydrogen, with 1 electron, has a circular orbit $n = 1$, $l = 0$. He, with 2 electrons, has a pair of orbits with $n = 1$, $l = 0$, $m_s = \pm\frac{1}{2}$ and therefore zero moment; it is chemically inert and from then on is inviolate as a closed K shell or group. Li, with 3 electrons, has a closed group for $n = 1$ with the helium-like electrons in the K shell. The third electron goes to the $n = 2$ or L shell. In the normal atom it takes on an orbit with $l = 0$, $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$. This is an elliptical orbit with $\frac{1}{2}$ a Bohr unit of moment of momentum. Be, with $Z = 4$, has 2 electrons while these can have $l = 0$ or $l = 1$ and $m_s = \pm\frac{1}{2}$; this other electron in the normal atom also goes to an orbit of $l = 0$ with 1 electron with $m_s = \frac{1}{2}$, the other with $-\frac{1}{2}$. Boron with $Z = 5$, has the 2 electrons in the $n = 1$ shell and 2 electrons with $n = 2$, $l = 0$, the third electron going to one of the $l = 1$, 3 m_l orbits where $m_l = -1$, 0, $+1$, and having $m_s = \pm\frac{1}{2}$ in each. Other electrons up to five more can be added as Z increases, thus closing the $n = 2$ or L shell, and with neon giving a stable grouping with 2 electrons of $l = 0$ and 6 electrons of $l = 1$ in that shell. This second group has a stable *octette* of $2 + 6$ electrons in the $n = 2$ shell outside of the $n = 1$ shell. Thus neon, with $Z = 10$ and closed groups of 2 K electrons and 8 L electrons, is the next inert gas. Thereafter, as Z increases, more electron shells add on with $n = 3$. Before the 18 electrons have all added on to give the closed $n = 3$ or M shell with 2 s, 6 p and 10 d electrons, the atom with increasing Z adds on the 2 s-type and 6 p-type electrons in an element with $Z = 18$, having a stable octette with zero moment and giving the inert gas argon. Thereafter as Z increases the next 2 s electrons of the $n = 4$ or N shell add outside the octette, giving K and Ca before the atom Sc starts to complete the incomplete $n = 3$ shell by beginning to add on the 10 remaining $n = 3$ or M electrons. This filling in process

starts the first *long period* of the periodic table, which period is complete only when with Kr, an inert gas, in which the 10 $n = 3$ or M electrons have closed the M shell in Cu and added 7 more electrons to complete an octette in the $n = 4$ or N shell, beyond the closed $n = 3$ shell. Thus in Kr one has the closed $n = 1$ shell of 2 electrons (K shell), a closed $n = 2$ shell of 8 electrons (L shell), a closed $n = 3$ shell of 18 electrons (M shell), and an octette of zero moment in the s- and p-type orbits in the $n = 4$ (N shell). This corresponds to an element with $Z = 36$, which is krypton. In general, following the closing of a shell, the next stable element has an octette, and, following this, 2 electrons of the next quantum orbit add on before the next inner shell fills in and starts to close. This brief summary suffices to show how quantization enables one to build up the electronic structure of the atom and to correlate the electron arrangements with spectroscopic terms. It remains now briefly to see how the spin moment and orbital moment affect the magnetic phenomena in gases.

As was stated earlier, the electron in a Bohr orbit of the simplest type should have a moment of momentum $p = h/2\pi$ and a magnetic moment $\mu = he/4\pi m$, so that $\mu = p\frac{e}{2m}$, or $\mu/p = e/2m$. This ratio μ/p is of great importance, as it appears in the studies from the Zeeman effect and in the atomic magnetic experiments such as the Barnett[27] and Einstein-deHaas[45] effect. In the simple Bohr theory these measurements *should* yield $\mu/p = e/2m$. Actual measurements have yielded the value $\mu/p = e/m$ and other values in spectroscopic work. Thus, before the electron spin was discovered, it was customary to write the equation $\frac{\mu}{p} = g\frac{e}{2m}$, or frequently $\mu/p = g$, where g represented the number of Bohr units $e/2m$ in the ratio μ/p. The spectroscopic use of the factor g was due to Landé and is named, after him, the Landé splitting factor. The quantity g here used is a pure number and multiplies into $e/2m$ to give μ/p. In some texts g is given as $\mu/p = g$, where g *implies the number* of Bohr units. For a classical electron orbit with no electron spin, $g = 1$. Actually the value of μ/p in some of the Zeeman effect data and in the Barnett and Einstein-deHaas experiments was found to be $\mu/p = e/m$. This means that in $\frac{\mu}{p} = g\frac{e}{2m}$, the quantity g has the value 2. It was this circum-

stance that led Uhlenbeck and Goudsmit to conclude that the electron must have an intrinsic spin moment s, given by $s = \frac{1}{2}(h/2\pi)$ and a magnetic moment $\mu_e = \frac{e}{2m}\frac{h}{2\pi}$. In this event for a free electron $\mu/p = \mu_e/s = e/m$, making $g = 2$ for the electron alone. In using the equations, it must be understood that e is expressed in electromagnetic units. If it were in electrostatic units, the equation for μ would be $\mu = \frac{e}{2mc}\frac{h}{2\pi}$, and $\frac{\mu}{p} = g\frac{e}{2mc}$, where c is the velocity of light. The fact that $g = 2$ in gyromagnetic experiments indicates that in these phenomena observed in ferromagnetic materials in order to magnify the feeble effects, the phenomenon is one due to the *spin moments of free electrons*, since the orbital moments do not appear in the value of g. Wave mechanics has evaluated g in terms of the atomic quantum numbers J, S, and L as

$$\frac{2m}{e}\frac{\mu}{p} = g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

It is seen that, if, as originally assumed for the simple Bohr orbit before the spin was known, $S = 0$, $L = 1$, and $J = 1$, g is 1, while in reality for a true Bohr orbit with electron spin $S = \frac{1}{2}$, $L = 0$, $J = \frac{1}{2}$, g is 2. For the Dy^{+++} ion, $g = \frac{4}{3} = 1.33$. A study of the gyromagnetic effect of Dy_2O_3 by Sucksmith[47] gave $g = 1.28 \pm 0.07$, which is in good agreement with theory.

A final test of the assumptions was made before the electron spin was shown to follow from the wave mechanics by Dirac. This lay in the development by Stern and Gerlach[28,29] of the magnetic deflection of molecular beams of silver atoms. Silver atoms like Li and K, used later by Meissner and Scheffers,[43] are atoms having an inner structure of closed electron shells with one external valence electron. In such atoms these electrons are such that the orbits are of the s type and as these are the only moments present, the atom is one showing the characteristics of the S type. In these atoms the value of L is 0, and $S = \pm\frac{1}{2}$. Hence, in this case, J will take on values of $\pm\frac{1}{2}$ of a Bohr unit in a magnetic field. This gives g a value of 2 and further implies that an atom of silver will orient itself in the magnetic field with its magnetic axis parallel or antiparallel to the field direction. The value of μ will thus be that of the

single Bohr magneton and will be given by $\mu_B = \frac{eh}{4\pi m}$. In general the magnetic moment of an electron in an orbit is given by $\mu = g\frac{ep}{2m}$, where p is the moment of momentum of the electron. On elementary quantum theory, $p = jh/2\pi$ where j is the magnetic quantum number. Wave mechanics, however, more accurately gives $p = \frac{h}{2\pi}\sqrt{j(j+1)}$. Hence actually $\mu = g\frac{e}{2m}\frac{h}{2\pi}\sqrt{j(j+1)}$. Calling $\mu_B = \frac{eh}{4\pi m}$ the unit of magnetic moment, $\mu = g\sqrt{j(j+1)}\mu_B$. The quantity μ_B is called the Bohr magneton and is the unit of magnetic moment. The numerical value of this unit can be computed at once from the equation, remembering the fact that the equations as given require e to be in electromagnetic units. The value, as given by Birge[49] as derived from the value of e/m from spectroscopic data, is $\mu_B = 0.9174 \pm 0.0013 \times 10^{-20}$ erg gauss^{-1}, which gives as the moment per mole $\mu_B N_A = 5{,}563 \pm 10$ ergs gauss^{-1} mole^{-1}. This should be the natural unit of magnetic moment and is derived entirely from theory. Pierre Weiss, from a study of magnetic susceptibilities per gram, determined a unit of magnetic moment whose value 1,123.5 ergs gauss^{-1} mole^{-1} is about $\frac{1}{5}$ of a Bohr magneton. This was done by evaluating the Curie constant C_M for each species and from this computing μ_W. The values of μ_W per mole or per atom for various substances were then tabulated. On the assumption that like the electron in electrical quantities there was a unit of magnetic moment, Weiss studied the values in the table and derived the figure given above as the *least common divisor* and thus assumedly the unit magnetic moment, the magneton. Actually all substances so far measured have more than this unit moment, the lowest being Ni with three units, other substances having in excess of five. In general the factor P is used to designate the magnetic moment in terms of Weiss magnetons, where $P = \sqrt{3RC_M}/1{,}123.5$ is expressed in terms of the molar magnetic moment derived from the Curie constant per mole C_M (see Sec. 100). Since it is possible for the total magnetic moment of an atom on the Bohr theory to have been caused by a combination of vectors which give a total moment less than the Bohr magneton, *e.g.*, Tl has $\frac{1}{3}$, it is clear that there is no discrepancy of a serious nature

between the two units. The Weiss magneton as 1,123.5 is, however, a fortuitous accident derived from scant data. That the Bohr magneton is, within experimental error, an integral multiple of the Weiss magneton is essential. Thus, while the Weiss magneton is an experimental convenience, the theoretically justified magneton is that of Bohr. It is in no sense a unit of observed atomic magnetism, as is the electron, the observed unit of atomic electricity, since the vector nature of the moment and quantization can produce resultant atomic moments less than the magneton.

In 1921 Stern,[28,29] in collaboration with Gerlach, applied his method of molecular beams to a direct attempt to determine whether magnetic moments of atoms were quantized in space or whether they were not, and to dispel the doubt as regards the validity of the Bohr magneton in contrast with that of Weiss. The device used was exceedingly simple. An atomic beam as described in Sec. 79 from an oven O of Fig. 69 carefully defined by a system of rectangular slits whose length was perpendicular to the plane of the figure was projected into the region between two pole pieces of a magnet. The beam in vacuum was parallel to the length of the pole pieces, one of which was a knife edge, the other pole piece being plane except for a rectangular channel parallel to the knife edge and opposite it. This gave a magnetic field perpendicular to the beam which was highly divergent such that the rate of change of field strength with distance across the poles, $\partial H/\partial Z$, was of considerable magnitude. Above the pole pieces was a plate P to receive and record the impinging atoms, or in work with alkali metals there was the slit of a hot-wire positive-ion pressure gage, which could be moved along the Z-axis to determine the intensities of the beam at various points. The value of $\partial H/\partial Z$ could be measured by means of a calibrated Bi spiral. The length of the beam in the field was known, and the velocity distribution of the atoms of the beam in the field could be determined from the temperature of the oven and Maxwell's law. One may designate the magnetic moment of the atom by μ. An atom of moment μ on entering the field will have a force exerted on it of magnitude given by $f = \mu \frac{\partial H}{\partial Z} \cos(\mu, H)$ where $\cos(\mu, H)$ is the cosine of the angle between μ and H. This assumes that μ is not influenced by the field. Practically μ is

the intrinsic magnetic moment of the atom, although the feeble moment induced due to the diamagnetic action acts to modify μ very slightly. This is seen by comparing the value of μ for diamagnetic action in a field H of some 10^3 gauss with the value for a Bohr magneton. It will be seen at once that the magneton is vastly larger than the induced moment. If now the moments μ are oriented in all directions in space, and the field does not alter the orientation appreciably, the atoms will be acted on by a force f varying from $\mu\frac{\partial H}{\partial Z}$ through 0 to $-\mu\frac{\partial H}{\partial Z}$. If, however, space quantization takes place as the Bohr theory demands, since J is $\pm\frac{1}{2}$ due to spin moments alone, L being 0, the atoms will in a very short space of time[50] all orient themselves either with the magnetic moments parallel to the field or antiparallel (north pole toward the S magnetic magnet pole or *vice versa*). In this case (μ, H) is 0 or 180, cos (μ, H) is $+1$ or -1, and $f = \pm\mu\frac{\partial H}{\partial Z}$. These atoms then traverse a distance x in the field from slit to collecting plate P under a force at right angles to their path given by f and an acceleration equal to f/m, where m is their mass. Thus they will be deflected a distance z given by $z = \frac{1}{2}\frac{f}{m}t^2$ from the position on P in the absence of H, where t is the time taken to go the distance l in the field. Now the velocity $c = l/t$ and $t = l/c$. Hence $z = \frac{1}{2}\frac{\mu}{m}\frac{\partial H}{\partial Z}\cos(\mu, H)\frac{l^2}{c^2}$. The velocity c is distributed among the atoms escaping from the oven by the Maxwell law according to the relation $N_c = \frac{2N}{\alpha^4}c^3e^{-\frac{c^2}{\alpha^2}}dc$, where α is the most probable velocity corresponding to the oven temperature. In consequence of this reasoning, if the classical concept is correct, a very diffuse pattern will result on the plate, due to the distribution of the values of the angle between μ and H among the atoms plus the fact that all atoms having a given angle will be deflected an amount z, dependent on c. Thus the density of the deposit as a function of z for any value of z will depend on the number of molecules having a given c which at the same time have a given angle between μ and H and thus bring them to that point on P. On the other hand, on space quantization there will be two values of z corresponding to the expression

$$z = \pm\frac{1}{2}\frac{\mu}{m}\frac{\partial H}{\partial Z}\frac{l^2}{c^2}.$$

and the numbers of molecules at each value of z will depend on the value of c which can bring the molecules to that point in the time l/c. Thus z will have a distribution to each side of the image of the slit in the absence of a magnetic field, whose maximum (*i.e.*, greatest density of deposit) will lie at z_α given by

$$z_\alpha = \pm\frac{1}{2}\frac{\mu}{m}\frac{\partial H}{\partial Z}\frac{l^2}{\alpha^2}.$$

A correction must in such experiments be made for finite slit width. Once this is made, the measurements of z_α, l, m, $\partial H/\partial Z$,

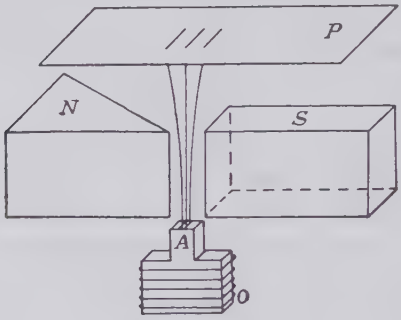

FIG. 69.

and α at once yield μ. Stern and Gerlach[28] actually performed this experiment using Ag. They found that in fact there was a splitting of the beam into two components and the value of z observed gave them a value of μ nearly equal to 1 Bohr magneton. A more recent result was obtained by Meissner and Scheffers,[48] using Li and K with an exceptionally high precision the density of deposit as a function of z being shown in the points of Fig. 27. They evaluated the Bohr magneton to 0.5 per cent. This astounding direct measurement of the magnetic moment of atoms at once establishes the correctness of the concept of spatial quantization, establishes the Bohr magneton, and, best of all, corroborates in a beautifully direct fashion the interpretation of orbital moments in terms of the electron spin. There is included below a table of results obtained in measurements of the moments of certain atoms in terms of Bohr magnetons by means of the Stern-Gerlach experiment and by means of spectroscopic studies.

	Atom								
	H	Na	K	Cu	Ag	Au	Zn	Cd	Hg
Stern-Gerlach.....	1	1	1	1	1	1	0	0	0
Spectroscopic.....	1	1	1	1	1	1	0	0	0

	Atom							
	Tl	Sn	Pb	Sb	Bi	Te	Ni	Fe
Stern-Gerlach.....	⅓	0	0	0	?	0	≥2	0
Spectroscopic.....	⅓	0	0	0	?	?	5	Large

From "International Critical Tables."[51]

References

1. Gladstone and Dale: *Phil. Trans. Roy. Soc.*, p. 8, 1858; p. 523, 1863.
2. Landolt: *Pogg. Ann.*, **123**, 595, 1864.
3. Lorenz: *Wied. Ann.*, **11**, 70, 1880.
4. Lorentz, H. A.: *Wied. Ann.*, **9**, 641, 1880.
5. Clausius: "Collected Papers," vol. 2, p. 135, 1876.
6. Nernst: "Theoretical Chemistry," 7th ed., Chap. VI, Macmillan & Co., Ltd., London, 1916.
7. Debye, P.: *Phys. Z.*, **13**, 97, 1912.
8. Debye, P.: Marx's "Handbuch der Radiologie," vol. 6, p. 597 ff., Leipzig, 1925.
9. Lorentz, H. A.: "Theory of Electrons," p. 138, Teubner, Leipzig, 1909.
10. Born; M.: "Encyclopedie der Mathematischen Wissenschaften," vol. 4, p. 758 ff.
11. Zahn: *Phys. Rev.*, **24**, 400, 1924.
12. Pauli, W., Jr.: *Z. Physik*, **4**, 319, 1921.
13. Hund, F.: *Z. Physik*, **31**, 81, 1925.
14. Smyth, C. P.: "Polar Molecules," Appendix I, Chemical Catalog Company, New York, 1931.
15. Sommerfeld: "Atomic Structure and Spectral Lines," Chap. IX.
16. Du Bois and Honda: *Verst. Amsterdam Akad.*, **18**, 666, 1910.
17. Owen, M.: *Ann. Physik*, **37**, 657, 1912.
18. Curie, P.: *Ann. Chim. Phys.*, **5**, (7), 289, 1895.
19. Langevin, P.: *J. Physique*, **4**, 678, 1905; *Ann. Chim. Phys.*, **5**, (8), 70, 1905.
20. Woltjer, H R., and Kammerlingh-Onnes, H.: Comm. Phys. Laboratory Leiden No. 167*c*, *Verst. Amsterdam Akad.*, **32**, 722, 1923.
21. Stoner, E. C.: *Loc. cit.*, p. 45.
22. Stoner, E. C.: *Loc. cit.*, p. 48.
23. Uhlenbeck and Goudsmit: *Naturwissenschaften*, **13**, 953, 1925; *Nature*, **117**, 264, 1926.

24. Dirac, P. A. M.: *Proc. Roy. Soc.*, **117,** 110, 1928.
25. Sommerfeld, A.: "Atombau und Spektrallinien," 5th ed., Chap. II, Sec. 4, p. 92 ff., F. Vieweg und Sohn, Braunschweig, 1931.
26. Russel and Saunders: *Astrophys. J.*, **61,** 38, 1925.
27. Barnett, S. J.: *Phys. Rev.*, **17,** 404, 1921; **20,** 90, 1922; **6,** 239, 1915; *Phys. Z.*, **24,** 14, 1923.
28. Stern and Gerlach: *Z. Physik,* **8,** 110, 1921; **9,** 349, 353, 1922; **41,** 563, 1927.
29. Gerlach and Stern: *Ann. Physik,* **74,** 45, 1924.
30. Debye, P.: "Polar Molecules," Chap. IX, Sec. 30, p. 169 ff., Chemical Catalog Company, New York, 1929. (Dover Reprint)
31. Van Vleck, J. H.: *Phys. Rev.*, **29,** 727, 1927; **30,** 31, 1927.
32. Wrede, E.: *Z. Physik,* **44,** 261, 1927.
33. Estermann, I.: *Z. Phys. Chem.*, **1,** 161, 1928; **2,** 287, 1929; *J. Chem. Phys.*, **1,** 390, 1933.
34. McMillan, E.: *Phys. Rev.*, **42,** 905, 1932 (abstract).
35. Stuart, H. A.: *Z. Physik,* **55,** 358, 1929; **59,** 13, 1929; **63,** 533, 1930; **80,** 107, 1933; see also *Z. Phys. Chem.*, **6,** 163, 1929; **17,** 429, 1932.
36. Stoner, E. C.: "Magnetism," p. 28, Methuen & Co., London, 1930.
37. Van Vleck, J. H.: *Phys. Rev.*, **31,** 587, 1928.
38. Pauling, L.: *Proc. Roy. Soc.*, **114A,** 181, 1927.
39. Hartree, D. R.: *Proc. Camb. Phil. Soc.*, **24,** 89, 1928.
40. Stoner, E. C.: *Loc. cit.*, p. 30.
41. Kobeko and Kurtschakow: *Z. Physik,* **66,** 195, 1930.
42. Heisenberg, W.: *Z. Physik,* **69,** 287, 1931.
43. Stoner, E. C.: *Loc. cit.*, p. 5 ff.
44. Catalan: *Phil. Trans. Roy. Soc.*, **223,** 127, 1922.
45. Einstein and de Haas: *Verh. Deut. Phys. Ges.*, **17,** 152, 1915.
46. See references in Harnwell and Livingood: "Experimental Atomic Physics," at bottom of p. 237, McGraw-Hill Book Company, Inc., New York, 1933.
47. Sucksmith, *Proc. Roy. Soc.*, **128,** 276, 1930; **133,** 179, 1931.
48. Meissner and Scheffers: *Phys. Z.*, **34,** 48, 1933.
49. Birge, R. T.: *Rev. Mod. Phys.*, **1,** 1, 1929.
50. Phipps and Stern: *Z. Physik,* **73,** 185, 1933.
51. "International Critical Tables," vol. 6, p. 346, McGraw-Hill Book Company, Inc., New York, 1929.

Books Recommended

a. Debye, P.: Marx's "Handbuch der Radiologie," vol. 6, p. 597 ff., 1925.
b. Debye, P.: "Polar Molecules," Chemical Catalog Company, New York, 1929. (Dover Reprint)
c. Smyth, C. P.: "Dielectric Constant and Molecular Structure," Chemical Catalog Company, New York, 1931.
d. Errera, J.: "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, 1928.
e. Stoner: "Magnetism," Methuen & Co., London, 1930.
f. Harnwell and Livingood: "Experimental Atomic Physics," p. 237 ff., McGraw-Hill Book Company, Inc., New York, 1933.

CHAPTER XI

APPLICATION OF THE KINETIC THEORY TO THE CONDUCTION OF ELECTRICITY IN GASES

102. Introduction.[1]—Probably one of the most spectacular applications of the kinetic theory has been in the field dealing with the conduction of electricity in gases. In fact, rather than this field being merely an application of the theory, it has done a great deal to assist in establishing it. With the discovery of X-rays, the problem attacked by Coulomb and many others unsuccessfully—of how the air conducted electricity—became open to quantitative investigation. This resulted from the considerable conductivity given the air and other gases by the X-rays and the later discovered radiations from radioactive substances. The intense interest excited by these rays led to rapid experimental advances, so that in a few years the following facts were established. The conductivity produced in gases by the agencies above consists in tearing loose from the neutral gas molecules negative electrons, leaving the residual molecule positively charged, or by liberating from a solid or liquid surface near the gas positively or negatively charged bodies. The positively charged bodies of molecular dimensions liberated by heat or radioactive disintegration are probably atoms that have lost an electron. The negative particles usually liberated by the action of heat, light, or a bombardment of the surface with electrical particles are the electrons. In most gases, the electron when liberated, after some time (the time being a property of the gas present and depending on the energy of the electron), will attach itself to a neutral molecule. It seems at present likely that both the positive molecule, after losing its electron, and the electron, after attaching to a neutral molecule, attract around themselves further molecules in view of the intense electrical fields present. These charged molecular groups in dry gases were early discovered to be the carriers of electricity in gases under ordinary conditions. They are called in analogy to the carriers of electricity in solutions the gaseous ions. The ions may be described and

studied largely by the velocities with which they move in an electric field. The motion of an ion in a gas under ordinary conditions in an electric field is a uniform velocity of drift. The velocity is proportional to the field strength X over a large range of field strengths (from a few tenths of a volt to 20,000 volts per cm) for a constant pressure. The velocity in cm/sec. in a field of 1 volt/cm is, therefore, a constant and is called the mobility. Besides the so-called normal ions, electricity is carried by two other sorts of carriers, electrons and large ions. The electron has a velocity which is not directly proportional to the field and which is thousands of times greater than that of the usual ions.[2,3,67] It can be measured only under particular conditions. The large ions are charged material particles—dust particles carrying charges. They are characterized by low velocities about one one-hundredth that of the normal gaseous ions. In spite of the claims of certain workers to have observed other classes of ions, the experiments do not warrant the acceptance of such conclusions.[4,5,6,22,69] In fact, if a gas is *really pure* it can be asserted that ions of one mobility only can be observed.[7,66,67] If, however, the gas has slight traces of an impurity for which the ion has a greater affinity than for the gas itself, there will be a transition period in which the ion is changing its nature, during which two mobilities will be observed, the ions giving these values occurring in relative proportions whose time variation marks the progress of the transition. Such cases were originally observed by Erikson[13] in air and have been critically studied by Bradbury.[66] In a heterogeneous gas such as poorly dried air with organic vapors, and subjected to chemical change in a closed space as a result of prolonged exposure to ionizing agents, a continuous distribution of ionic mobilities, *i.e.*, a mobility spectrum, can be expected after the lapse of considerable time. The existence of such a spectrum has been reported by numerous observers and has been accurately delimited by Zeleny[70] and Bradbury[67,69] in air under the conditions mentioned after 0.1 sec., the spectrum increasing in width and the most probable mobility decreasing as the ions aged and the faster ions disappeared due to recombination. These velocities vary from gas to gas and differ slightly for positive and negative ions in the same gas. The values have been determined by many different means and these agree fairly well in placing them in a range between about 7 cm/sec. per volt/cm (in H_2 gas where the velocity is greatest) to

about 0.2 cm/sec. per volt/cm (in vapors like ethyl ether where the velocities are lowest). The mobility of the ion for a given gas is inversely proportional to the density of the gas from nearly 100 atmospheres (atm.) down to a few mm of gas pressure. This did not seem to hold for negative ions in certain gases below 100 mm, but Wellisch[8] and Loeb[9] have shown that this is due to the complicating presence of free electrons and that the mobility of ions is even here inversely proportional to the pressure. The mobility reduced to constant gas density is known as the mobility constant. This constant appears to be almost independent of temperature except at the lowest temperatures studied, a decrease in the constant of 10 per cent being observed at liquid-air temperatures.* In general, the positive ion is slower than the negative ion, although in gases like HCl the reverse is true.[11] Newly generated positive ions, however, have a mobility equal to the negative ion in some gases where the final positive ion is slower.[71] The ions in most cases studied carry a single electrical charge and the Faraday constant for gas ions is closely that observed for univalent ions in electrolysis.[12,72] Usually, ions generated with a multiple charge lose all but one charge in the millions of molecular impacts they make in going the cm in the gas required for measurement.[14,72,81]

The mobility of the ion may be derived from the kinetic theory. In fact, an elementary deduction of this was given in Sec. 22 of Chap. III. The more rigorous derivations of this quantity on the kinetic theory, including certain complications introduced by the forces exerted by the charges on the ions, will form one of the portions of this chapter.

Closely allied to mobility and related to it by a simple relation is the coefficient of diffusion of the ions, that is, ions of one sign in a gas exert a partial pressure. If the forces due to the charges be ignored (as they may be when ions are present in low concentrations), they will then diffuse through the gas as a result of the partial pressure. As in molecular diffusion, the number diffusing per second N_1 across unit area normal to the concentration gradient $\frac{dn}{dz}$ is given by $N_1 = D\frac{dn}{dz}$, where D is the constant of diffusion governed by the kinetic theory. In ions, the equation

* The experimental results are somewhat contradictory on this point. But the later careful experiments of Erikson[10] seem to indicate the correctness of the present statement.

for gas molecules is complicated by the attractive forces on the ions. The relation between diffusion and mobility and the value of the coefficient of diffusion D merits being deduced from the kinetic theory.

Again, if ions are generated in a gas the positive and negative ions are present initially in equal numbers. If the charge in the gas is measured at once after the ionizing agent is cut off, a certain number present is obtained. If the number at varying time intervals after the ionization has ceased is measured, the number found decreases as the time increases. Experiment shows that, roughly at least, the equation representing this is

$$-\frac{dn}{dt} = \alpha n^2.$$

Here $-\frac{dn}{dt}$ is the rate of disappearance of ions, n is the number per unit volume present at any instant, and α is a constant characteristic of each gas, called the coefficient of recombination. The name of the constant indicates the nature of the cause of disappearance of the ions. Due to their mutually opposite charges and to diffusion, the positive and negative ions come within a close distance of each other. Thus in time they reunite in pairs and the ionization disappears. This process is called the recombination of the ions. The evaluation of the constant α in terms of the kinetic theory will be one of the tasks of this chapter.

The velocity of an electron in unit electrical field, as was said before, is not a constant, that is, the electron has, properly speaking, no mobility. It is convenient, however, to evaluate the velocity of the electron in the field as if it had a mobility and to study the deviations from this in terms of a kinetic-theory interpretation. The theory was first suggested by Townsend[15] and was later amplified by Loeb.[2] The final successful solution of the problem from a theoretical point of view was due to Compton.[3] It will be given in a separate section.

As was stated in the discussion of ionization, the electron liberated by the ionizing process eventually attaches to gas molecules in some gases to make ions.[16,17,18,73,74] A study of ion formation indicates that this so-called electron affinity of gas molecules can be characterized by a quantity n, the average number of impacts to cause attachments. The nature of n

described above indicates that it was derived by a kinetic-theory analysis. This will constitute another section of the chapter.

Finally, another phenomenon merits a brief treatment. If electrons be liberated from a plate in a rarefied gas, the current which they carry from this plate to one parallel to it but a finite distance away is a function of the voltage. As the voltage increases from zero, the current increases at first in a nearly linear fashion. It gradually, however, departs from linearity, the increase as the voltage increases becoming less. Eventually, it was believed to reach a constant or saturation value. This, in the case of photoelectrons, it does only in theory,[75] for before saturation is reached, a new mechanism appears. For thermionic sources with heavier currents, space-charge effects enter. As higher fields are applied, the apparent saturation gives place to a new rapid increase of current with potential, the current eventually increasing exponentially toward infinity as a spark. The explanation given is that in this region the electrons move so fast that they are able to remove the electrons from the gas molecules which they strike. Thus each electron may make α new pairs of ions per cm path and the current increases with distance in the gas according to a law $i = i_0 e^{\alpha x}$, where α is the number of new ions formed per cm of path, x the path, and i_0 the initial current. Now α is a function of the pressure and field strength. It depends on the ability of the electron to pick up energy from the field and the probability of its ionizing once it has this energy. An expression for α was deduced by Townsend.[19] In view of the recently acquired knowledge of electron kinetics in a gas this theory must be revised, and the kinetic-theory analysis of it furnishes an excellent means of attack.

Thus the application of the kinetic theory to the field of gaseous ions presents many new and interesting investigations, and it is the purpose of this chapter to set forth the salient features of some of them as briefly and clearly as possible.

103. The Kinetic-theory Analysis of Gaseous-ion Mobilities, Assuming Ions That Are Charged Clusters of Molecules Exerting No Forces on the Gas Molecules Due to Their Charge.—The elementary treatment of gas-ion mobilities was given in Sec. 22. The treatment to be given here is on the strict classical kinetic theory. It was due initially to Langevin,[20] but the treatment

here given is a modification of it given by H. F. Mayer[21] in a critique of the Langevin theory.*

The assumptions underlying this derivation are that the ion is a group of molecules of total mass m which moves in an electrical field due to its charge e. In moving through the field, it is hampered by collisions with gas molecules of mass M, to which by elastic impacts it is continually losing the momentum it

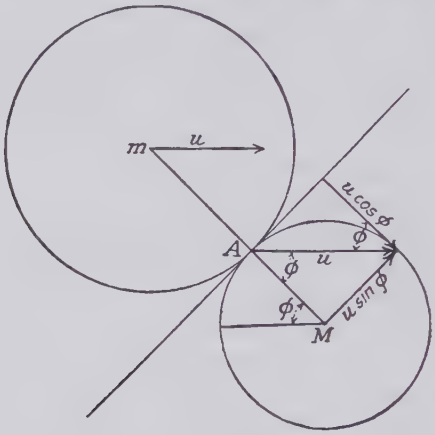

FIG. 70.

has gained in the direction of the field. It exerts no attractive forces on the molecules and both ions and molecules are, for simplicity, assumed spherical. The velocity gained from the field between impacts is further supposed small compared with the thermal velocities of agitation.

Such assumptions lead one to the study of the interchanges of momentum in impact. Assume a molecule M at rest and let an ion of mass m move relatively to M with a velocity u. Assume that the point of impact be A (Fig. 70). The velocity may be resolved into two directions perpendicular and parallel to the surface of M at the point of impact. The tangential component is $u \sin \phi$, where ϕ is the angle between the normal to the surface at A and the direction of motion. The normal component is $u \cos \phi$. The latter component is altered by the impact, while the former is not. To this impact the laws of conservation of momentum and energy may be applied. These are

* A recent variant of this derivation of probably greater classical precision is due to Compton. It is given *in extenso* in *Rev. Mod. Phys.*, **2**, 204–218, 1930.

$$mu \cos \phi = mu_1 + MV,$$
$$\frac{1}{2}m(u \cos \phi)^2 = \frac{1}{2}mu_1^2 + \frac{1}{2}MV^2,$$

where u_1 is the velocity of m after impact and V is the velocity of M after impact, the initial velocity of M having been 0. Solving for u_1, one obtains $u_1 = \frac{m - M}{m + M}u \cos \phi$. After impact, therefore, the velocity of m is composed of the two components at right angles, $u \sin \phi$ and $\frac{m - M}{m + M}u \cos \phi$. These give a resultant velocity u' of m along the initial direction of motion, that is, the body m persists in its motion in the direction of its motion before impact with a velocity u'. This velocity is given by adding

$$(u \sin \phi) \sin \phi + \left(\frac{m - M}{m + M}u \cos \phi\right) \cos \phi,$$

with the result that

$$u' = u\left(\sin^2 \phi + \frac{m - M}{m + M} \cos^2 \phi\right).$$

The average persistence is found by taking the average of u' for all values of ϕ. This is done by multiplying by the chance of an angle ϕ, between ϕ and $\phi + d\phi$, which is $2 \sin \phi \cos \phi d\phi$, and integrating ϕ from 0 to $\pi/2$. Hence,

$$\bar{u}' = 2u \int_0^{\frac{\pi}{2}} \left(\sin^2 \phi + \frac{m - M}{m + M} \cos^2 \phi\right) \sin \phi \cos \phi d\phi.$$
$$\bar{u}' = \frac{m}{m + M}\, u = \mu u,$$

where

$$\mu = \frac{m}{m + M}.$$

If the molecule M was not at rest but had components of motion U, V, and W, while the ion m had components u, v, w, the u and u' used before would be replaced by the relative velocities $u - U$ and $u' - U$. These lead at once to a value of $\bar{u}' = \frac{mu + MU}{m + M}$. Similar relations hold for v' and w', the velocities along the v- and w-axes after impact. The average loss of velocity in impact is, therefore,

$$u - \bar{u}' = \frac{M}{m + M}(u - U).$$

For simplicity, assume that all of the N gas molecules in unit volume have the velocity components U, V, W, while the gas ion moves through the gas with the uniform velocity components u, v, w. The number of impacts per second suffered by the ion is then given by the mean collision frequency, which is given by $\pi s^2 N c$. Here $s = r + R$, the sum of the radii of ion and molecules, and c is the relative velocity of the ion and the molecules. This is given by

$$c = \sqrt{(u - U)^2 + (v - V)^2 + (w - W)^2}.$$

The loss of velocity of the ion m per second with the number of collisions per second given above is

$$(u - \bar{u}')Ns^2\pi c.$$

Now the velocity components of the molecules are not all equal, and the components of the ion change at each impact. If df be the chance that the ionic velocities lie between u and $u + du$, v and $v + dv$, and w and $w + dw$, and if dF be the chance that the molecular velocities U, V, and W lie between U and $U + dU$, V and $V + dV$, and W and $W + dW$, then the mean loss of the velocity of the ion per second in its path through the gas is given by

$$\int\int (u - \bar{u}')\pi s^2 N c df dF.$$

The ion, on the other hand, is gaining a velocity each second along the u-axis from the force exerted by the field on its charge. Call this increase in velocity per second $b = K/m$, that is, b is the acceleration of the ion, K is the force, and m the mass of the ion. At equilibrium the ion is moving with a uniform velocity of drift, and hence the *average discontinuous decelerations* due to impacts must equal the continuous acceleration due to the field. Thus

$$mb = K = m\int\int (u - \bar{u}')N\pi s^2 c df dF,$$

or

$$K = \frac{mM}{m + M}\int\int (u - U)N\pi s^2 c df dF.$$

If the gas, as a whole, is at rest, that is, if mass motion is absent, df and dF can be replaced by their equivalents in the Maxwell

distribution law. This law expressed, using the Boltzmann constant h (see Sec. 36), gives for df and dF the values,

$$df = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm[(u-\omega)^2+v^2+w^2]} dudvdw$$

where ω is the average velocity of drift of the ion in the u direction.

$$dF = \left(\frac{hM}{\pi}\right)^{3/2} e^{-hM(U^2+V^2+W^2)} dUdVdW.$$

Since ω is very small compared to u (some tens of cm per second compared to 4×10^4 cm per second or more), the higher powers of $\frac{\omega}{u}$ can be neglected, and so

$$df = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(u^2+v^2+w^2)}(1 + 2hmu\omega) dudvdw,$$

Putting these quantities into the expression for K, on integration,

$$K = \frac{4\omega}{3} N\pi s^2 \sqrt{\frac{4}{h\pi}\frac{mM}{m+M}}.$$

The integrations above are more easily accomplished if the new variables below are used.

$$u = X + \frac{M}{m+M}x, \qquad U = X - \frac{m}{m+M}x,$$

$$v = Y + \frac{M}{m+M}y, \qquad V = Y - \frac{m}{m+M}y,$$

$$w = Z + \frac{M}{m+M}z. \qquad W = Z - \frac{m}{m+M}z.$$

$$dudvdwdUdVdW = dxdydzdXdYdZ.$$

From the equation after integration one has at once the velocity of the ion ω as

$$\omega = \frac{3}{4}\frac{K}{\pi s^2 N}\sqrt{\frac{h\pi}{4}\frac{m+M}{mM}}.$$

This is a general equation and makes it possible to obtain either the mobility or the diffusion coefficient. If the K above designates the force on an ion Xe, where X is the field strength and e is the charge, ω is the velocity of the ion in the field. If K is the force on the ion due to the partial pressure of the ions, ω is the velocity of diffusion of the ions.

To reduce the expression for the mobility of the ion to a handier form, K may be replaced by eX, and it should be remembered that the square of the average speed $\bar{c}^2$ is equal to $4/(\pi hM)$ for the molecules. Thus

$$\omega = \frac{3}{4}\frac{eX}{\pi s^2 N}\frac{1}{\bar{c}M}\sqrt{\frac{m+M}{m}}.$$

If one had used $(\bar{c}')^2 = 4/(\pi hm)$ for the *ions*, one would have

$$\omega = \frac{3}{4}\frac{eX}{\pi s^2 N}\frac{1}{\bar{c}'m}\sqrt{\frac{m+M}{M}}.$$

$\bar{c}$ and $\bar{c}'$ may be replaced by C and C' for the molecules and ions, that is, by the square roots of the mean square speeds, by remembering that $\bar{c} = \dfrac{C}{\sqrt{3\pi/8}} = \dfrac{C}{1.085}$ (see Sec. 35). Again, $1/(\pi N s^2)$ may be called the mean free path of the ion in the gas. This is not strictly true, as may be seen from Secs. 17 and 37. $1/(\pi s^2 N)$, however, may be replaced by the symbol λ and, for short, designated as the mean free path. The equations above become, on making these changes,

$$\omega = 0.815\frac{Xe\lambda}{MC}\sqrt{\frac{m+M}{m}}$$

and

$$\omega = 0.815\frac{Xe\lambda}{mC'}\sqrt{\frac{m+M}{M}}.$$

Since $\omega/X = k$, the mobility of the ion,

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}},$$

$$k = 0.815\frac{e}{m}\frac{\lambda}{C'}\sqrt{\frac{m+M}{M}}.$$

Mayer, in the article where this derivation is given, deduces the expression of Lenard from the reasoning applied here. The only essential difference, according to Mayer, is the fact that Lenard takes into account the possibility of the velocity in the direction of the field between impacts being great relative to the velocity of agitation, due to the field becoming appreciable. In general, this correction is not necessary. Its introduction complicates the derivation and makes discussion of a more involved

equation tedious. As neither of these theories is entirely correct, the small difference is of no importance. In any case, the only essential change is one in the mass factor. Both forms of the equation deduced above are useful. They give the mobility of the ion in terms of the charge and free path of the ion divided by the mass and root mean square of the velocity of the gas molecules in one case, and divided by the mass and root-mean-square velocity of the ion in the other case. The first equation is best in discussing the value of the mobility of the ion, as C and M are known and the factor for the mass of the ion changes k but little. The second equation makes it possible to carry the equation over to a carrier like the electron for further discussion, for all that is needed is to introduce the values for λ, C', and m for an electron into the equation.

To deduce the expression for the coefficient of diffusion of ions, the force K must be determined in terms of the diffusion coefficient. The expression for the number of ions n diffusing across 1 cm^2 of area per second is given by

$$n = D\frac{dn'}{du},$$

where n' is the number of ions per cm^3, dn'/du is the gradient in the u direction, *i.e.*, the direction of diffusion, and D is the coefficient of diffusion. Call ω the velocity of diffusion along u. Then $n = \omega n'$, or $\omega = \frac{D}{n'}\frac{dn'}{du}$. If the ions exert a partial pressure, as gas molecules do, one may write that $p = an'$, where a is a constant, and $dp = adn'$. Thus $dp/p = dn'/n'$. The only doubt about this approximation is that the charges of the ions exert a force of repulsion on each other. For gaseous-ionization experiments, charge densities of more than 10^6 ions per cm^3 are rare. This separates the ions, on the average, by distances of the order 5×10^{-3} cm from each other. The forces of repulsion at this distance, even on an inverse-square law, are small and may be neglected in some cases. Replacing dn'/n' by its equivalent, one has the velocity of diffusion given by

$$\omega = \frac{D}{p}\frac{dp}{du}.$$

Now the force acting on the ions is the pressure times the area. Since the number of ions n diffusing was taken per unit area, the force on a cm^3 of ions due to the pressure gradient dp/du is

$$\frac{dp}{du} \times 1 \text{ cm} \times 1 \text{ cm}^2,$$

that is, the force on 1 cm^3 of ions is dp/du. The force on one ion will be

$$\frac{1}{n'}\frac{dp}{du} = K = \frac{p\omega}{n'D}.$$

Placing this into the expression for ω,

$$\omega = \frac{3}{4}\frac{\frac{p\omega}{n'D}}{\pi s^2 N}\sqrt{\frac{h\pi}{4}\frac{m+M}{mM}},$$

calling $1/(\pi s^2 N) = \lambda$, and inserting M and C for molecules for h,

$$D = 0.815\frac{p\lambda}{n'MC}\sqrt{\frac{m+M}{m}}.$$

Since $p/n' = \frac{1}{3}m(C'^2) = \frac{1}{3}MC^2$ if ions exert a gas pressure,

$$D = 0.815\,\frac{\lambda C}{3}\sqrt{\frac{m+M}{m}}.$$

For $m = M$,

$$D = 0.815\,\frac{1.41}{3}\,\lambda C = 0.384\lambda C.$$

The equation for the diffusion of molecules where the masses were the same as the masses of the molecules diffused into was found on simple kinetic theory to be $D = \frac{1}{3}\bar{c}L$. Since $L = 1/(\sqrt{2}\pi\sigma^2 N)$, $\lambda = L\sqrt{2}$ and the above equation becomes $D = 0.217\lambda C$, which is roughly the same as the one for ions. If the expression for the mobility of the ion from this equation be divided by the expression for D,

$$\frac{k}{D} = \frac{0.815\,\frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}}}{0.815\,\frac{C}{3}\lambda\sqrt{\frac{m+M}{M}}},$$

then $k/D = 3e/MC^2$. Multiplying top and bottom of the right-hand side of the equation by N, the number of molecules per cm,^{3} then

$$\frac{k}{D} = \frac{Ne}{\frac{1}{3}NMC^2} = \frac{Ne}{P},$$

that is, the mobility k divided by the diffusion coefficient D is the Faraday constant divided by 22,400 and the pressure P corresponding to N. If the value of e for gaseous ions is the same as for electrolytic ions the quantity Pk/D should give the Faraday constant for monovalent ions divided by 22,400. This is, in fact, the case. Experiment gives $k = 1.8$ cm/sec. per volt/cm* for negative ions in air, that is, 540 cm/sec. per e.s.u./cm, while it gives D for negative ions in air as $D = 0.043/\text{cm}^2 \times \text{sec.}$, when $P = 1 \times 10^6$ dynes per cm^2.

Thus $$P\frac{k}{D} = \frac{540 \times 10^6}{0.043} = 1.25 \times 10^{10} \text{ e.s.u.}$$

Now N is 2.71×10^{19}, and e is 4.77×10^{-10} e.s.u.; whence Ne is 1.29×10^{10} e.s.u. This agreement is well within the accuracy of the measurements of D. It is therefore possible to assume that ions exert a partial pressure like a gas, to assert that they carry the same charge as univalent ions, and to calculate D from k (measured by $D = 0.0236k$), when k is in cm/sec. per volt/cm.

104. Test of the Simple Ion Theory and Further Formulation of the Mobility Problem.—One more point in connection with diffusion of ions leads to a test of this theory. If the diffusion coefficient of ions in CO_2 is compared with the coefficient of molecules of N_2O into CO_2, a nearly equivalent case, it is found that D for these ions is 0.023, while for CO_2 molecules it is 0.15 to 0.1. Thus the ions diffuse about one-sixth as fast as the uncharged molecules.

This must mean that λ for the ions is not the same as for uncharged gas molecules. A discrepancy in a similar direction is brought out if k is computed for ions in air from the equation

$$k = 0.815 \frac{e}{M} \frac{\lambda}{C} \sqrt{\frac{m + M}{m}}.$$

For this purpose assume $M = m$, that is, that the ion has molecular dimensions. The λ here used is $\sqrt{2}$ times the L from kinetic theory for air molecules, and, as the $\sqrt{\frac{m + M}{m}}$ is $\sqrt{2}$ for the case where $M = m$, $k = 1.63 \frac{e}{M} \frac{L}{C}$. Putting in the accepted kinetic-theory values for L, M, C, and e a computed mobility for ions of 11.7 cm/sec. per volt/cm is obtained for air ions. The

* This value of k is the old value taken under conditions similar to those used in evaluating D. The true values differ by tens of per cent and the agreement above is fortuitously good.

observed value for air is 2.2 cm/sec. per volt/cm for negative ions and 1.6 cm/sec. per volt/cm for positive ions.[23,7] Again the mobility is nearly one-fifth that computed.

This can mean that the value of λ assumed, together with the other constants, is not that for charged molecules which do not exert any forces on neutral molecules in virtue of their charge as they move through the gas. The action of the charge of the ion on neutral molecules may be explained in two ways. The charge on the ion may attract neutral molecules in virtue of its field; that is, it may induce a charge on an uncharged molecule or it may act on electrical dipoles already present in the molecules (see Chap. X, Sec. 96). In doing so it will undergo exchanges of energy and momentum with these molecules, without impact. It may also suffer a decreased mean free path, as, owing to the attractive forces, an impact that was not predestined to occur had there been no forces will take place. This type of action can be explained as causing an apparent increase in s, the sum of the radii of ion and molecule due to the attractive forces. Thus, as s increases, λ, the free path, will decrease. Such a theory is known as the *small-ion* theory and was independently developed by Wellisch[24] and Sutherland[25] in 1909. The earliest explanation of the small mobility offered was the alternative to the view above, namely, that the charge on the ion was so intense that the neutral molecules were bound to the molecule with the charge and that this binding went on until the force field around the ion was practically ineffective beyond the ion. Such an ion is called the *cluster ion*. The number of molecules in the cluster has been estimated at from 6 to 30 molecules by various workers on different theories. The cluster formation would then change the factor $\sqrt{\frac{M+m}{m}}$ used above, and the increase in s^2 due to the cluster would make a corresponding decrease in λ.

The two points of view concerning the nature of the ion have been the cause of an unnecessarily bitter controversy for many years. As is usually the case in such controversies, neither side was exclusively correct. The experimental developments in the last seven years have done much to clarify the problem. It may safely be stated that the studies of mobilities in mixtures,[71,76] the investigations on the aging of ions[13,66,68,69,70] and the change in mobility with age,[77,78,79] and the investigations on ions soon after their formation by the mass spectrograph[80] have

shown the ions to be complex to the extent of being addition products of one or two and perhaps three active molecules to the charged carrier in close analogy to the definite complex ions in solution. Such ions are electrochemical combinations which depend on the sign of the charge and the active impurities present. Thus NH_3 and amines RNH_2 and ethyl ether go exclusively to the positive ion,[71] while alcohols, ROH, HCl, and Cl_2 are strongly attracted to the negative ions.[76] The aging experiments indicate a rapid transition,[13,66,68,69] taking place in a single step with *no intermediate products* when one ion changes to another. The rate of change depends on the relative stability of the two complexes and the relative proportions of the two molecular species competing for attachment present in the gas. There is absolutely no authentic evidence for the existence and gradual growth of ions by successive addition of molecules to clusters of one or more molecular layers (6 to 30 molecules) about the molecule carrying the charge. The effects of the complex ion formation are in magnitude no greater than the observed differences in the mobilities of positive and negative ions, though where large organic molecules are added, the effect may be notable.[76] They are not responsible for the general fivefold lowering of the mobility of the ion below that of the forceless molecules which, it can be shown, are due to a small-ion type of action.

The original controversy led back to the question of the force fields active in ion formation. If the forces are intense in the immediate neighborhood of the charged molecule, a clustering may be expected. If the forces are weaker but fall off more slowly with distance, the small-ion theory would appear to be the more correct. While the nature of the force between ion and molecule is the well-known inverse fifth power law of dielectric attraction which must hold at considerable distances from the charge, it is quite uncertain to what extent the law can be applied when charge and molecule are within one or two molecular diameters of each other.[71] This is unfortunately the critical distance for stable cluster formation so that at present from theory alone it is impossible to predict the nature of the ion. This, as will be seen, explains why the controversy has continued despite the fact that the general law of force could be predicted with more certainty than any of the force laws for molecular interaction used by the kinetic theory.

The inverse fifth power law of force between a charge and neutral molecule results from just the type of action discussed in the first half of Chap. X.[27] If a neutral molecule be brought into an electrical field, it will have an electric moment induced in it by the field, and if it already happens to be an electrical dipole, this dipole will be so acted on by the field that its average orientation with respect to the field gives it an *effective* moment in the same sense as the *induced* moment. In both cases the induced and effective moments are in proportion to the inducing field in the case of weaker fields, though this may not be the case in fields 10^{-8} cm from an ion. Such molecular electrical dipoles will be attracted in a divergent field, such as is produced by a single isolated charge on an ion, with a force inversely proportional to the cube of the distance from the ion and the strength of the effective dipole moment. Thus, since the effective dipole moment μ is proportional to the field r cm distant from a point charge, *i.e.*, proportional to $1/r^2$, while the dipole is attracted by a force proportional to μ/r^3, the charge will attract the ion with a force inversely proportional to the fifth power of the distance, *i.e.*, with a force proportional to $1/r^3 \times 1/r^2 = 1/r^5$. The law of force, it is seen, even though perhaps faulty, must form the basis for any quantitative discussion of ionic behavior. It is thus important that the law of force be deduced at this point.

The uniform field F at any point between two plates with a density of electrification of opposite signs σ is given by $F = 4\pi\sigma$. If a dielectric whose constant is D is placed between them, the field F' is now $F/D = F'$. This apparent loss of intensity is due to the absorption of the lines of force by charges in the dielectric, that is, it is due to a charge induced in the medium by the field and is proportional to it. Symbolically, this is designated by the relation

$$F - F' = 4\pi\sigma',$$

where σ' is the surface density equivalent to the charge produced on the material. From this it follows that

$$\frac{F - F'}{F'} = D - 1 = \frac{4\pi\sigma'}{F'},$$

or

$$\sigma' = \frac{F'(D - 1)}{4\pi}.$$

For a gas between the two plates σ', the charge density multiplied by the area of the plates and multiplied by the distance between them, or σ' times the volume between the plates, gives the equivalent electrical moment of all the charges in the gas. This divided by the volume of the gas between the plates then gives M, the electrical moments of the gas molecules between the plates per unit volume, that is, $\sigma' = M$, the moment of the polarized gas per unit volume. Hence one has $M = (D - 1)F'/4\pi$. Now the electrical moment of one molecule is $\mu = M/N$, where N is the Loschmidt number. Thus the moment of a molecule can be set as

$$\mu = \frac{(D - 1)F'}{4\pi N}.$$

Since in this case F', the acting field, is produced by a charged molecule (an ion), the field can be regarded (except at very small distances) as due to a charge located at a single point. F' is then given by e/r^2, where e is the charge and r the distance from the ion. Thus $\mu = \frac{(D - 1)}{4\pi N} \frac{e}{r^2}$. It is well known that for a dipole of moment μ the force with which it is acted on by a point charge r cm distant is given by $f = 2\mu e/r^3$.* Thus the force between ion and molecule is given by the expression

$$f = \frac{(D - 1)e^2}{2\pi N r^5}.$$

The potential energy of the ion at a distance r from the molecule due to the field is given by

$$W = -\int_r^\infty \frac{(D - 1)}{2\pi N} \frac{e^2}{r^5} dr = -\frac{(D - 1)}{8\pi N} \frac{e^2}{r^4}.$$

The potential is negative, which means that the work which the molecule can do in being moved to infinity is negative.

From this law of force it is possible to estimate the size of the ion cluster, for, in order to be stable, the cluster must have a sufficient radius so that r, the distance between the center of the ion and center of the molecule (assuming the law to hold at such distances), is small enough so that the potential energy of the ion and molecule is equal to the average energy of thermal agita-

* This assumes r to be large compared with μ/e.

tion. If the kinetic energy of agitation is greater than the potential energy, on the average, the molecule will not describe a closed orbit about the ion and thus it will not be captured and bound. Hence, for a cluster ion, the radius r_c must be such that W/KE, the potential over the kinetic energy, is greater than unity. Now $W = \frac{(D-1)e^2}{8\pi N r_c^4}$, and $KE = \frac{1}{2}M\dot{C}^2$, thus

$$\frac{W}{KE} = \frac{(D-1)e^2}{4\pi NMC^2 r_c^4} = \frac{(D-1)e^2}{12\pi p r_c^4},$$

since $p = \frac{1}{3}\dot{N}MC^2$. D for air is 1.0006, $p = 1 \times 10^6$ dynes per cm^2, and $e = 4.8 \times 10^{-10}$. If r_c be taken as $r_c = 3.3 \times 10^{-8}$, which is the value of the molecular diameter in air and corresponds to an ion composed of a layer of molecules one molecule deep about the central charged molecule, one obtains $W/KE = 3.1$. Thus a monomolecular layer cluster could be stable. Were the nucleus and molecules spheres of the same size, the maximum number of molecules in a stable cluster would be 12. A cluster of more than 12 molecules would require another layer, for 12 molecules is all that can be placed around a sphere of the same size. A larger cluster would perhaps be a little less than double r, for the next layer of molecules, and r^4 would be 16 times as great. This would give $W/KE = 0.19$, and the outer layer would not be stable. It is very unlikely that the ion cluster numbers more than 12 molecules, and evidence seems to point to possibly as few as one or two more or less permanent companions to the charged molecule.

105. Deduction of an Expression for the Shortening of the Mean Free Path Due to Attractive Forces—a Typical Small-ion Theory.—With the adoption of the law of force as probably obtaining in order of magnitude, it becomes possible to compute the force of attraction and consequently the apparent decrease of the mean free path of the ions due to such a law. In general, a method devised by Wellisch[24] will be used. Certain errors were inherent in the original deduction and they will, accordingly, be corrected for in this text. Certain objections to Wellisch's theory as a small-ion theory may also be urged. However, the equation as deduced is able to give mobilities of the correct order of magnitude without any arbitrary assumptions as to size of cluster and is thus an improvement on previous theories. It is also being included as it makes it possible to see

how ionic or intermolecular forces can influence the mean free path.* The more complete and correct mobility-equation derivations are entirely too involved to reveal the method of attack clearly and thus will not be derived, although their conclusions will be discussed.

Wellisch starts out with the mobility equation in its elementary form $k = \frac{e}{m}\frac{\lambda}{\bar{c}_1}$ and proceeds, after assigning λ the value for the mean free path of an ion of mass m in a gas of molecules of mass M, to find how the forces of attraction influence the mean free path. In the present deduction the equation of Langevin,

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}},$$

will be used as a basis, and the effect on λ of the forces of attraction between ion and molecule will be calculated as Wellisch

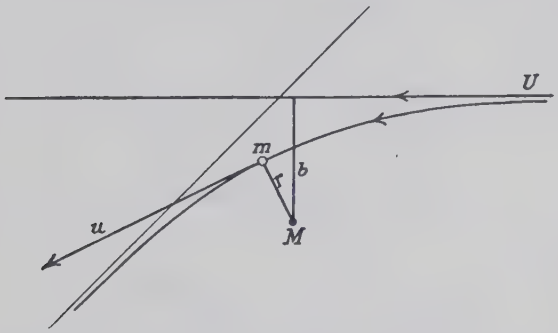

FIG. 71.

calculated them. The law of force between ion and molecule is $F = \frac{(D-1)e^2}{2\pi N r^5}$, as deduced above, where r is the distance between the ion and the molecule. This gives the potential energy at r, $W_r = \frac{(D-1)e^2}{8\pi N r^4}$. Consider, for simplicity, that the molecule is at rest and that the ion approaches it with the total relative velocity. Call U the velocity of the ion at infinity and u the velocity at the point of closest approach. The ion will come from infinity, increasing its velocity as it approaches, describe an orbit about the fixed molecule and depart, as it is not captured.

* This deduction parallels that of Sutherland Sec. (63) and without the complicated mathematics arrives at a similar result.

Where the ion and the molecule separate after the distance of closest approach, the orbit is an hyperbola, the initial velocity U being directed along the asymptote (see Fig. 71). The law of conservation of energy says that in such an encounter

$$\frac{1}{2}m(u^2 - U^2) = W',$$

where W' is the relative potential energy of the ion and the molecule. W' is related to the potential W, the actual potential energy of the ion given above, by a simple relation. Call M the mass of the molecule and C its velocity, while C_1 is the velocity of the ion of mass m. Then

$$W_r = \frac{mC_1^2}{2},$$

while

$$W' = \frac{mC_1^2}{2} + \frac{MC^2}{2}.$$

However,

$$mC_1 = MC,$$

or

$$C = \frac{m}{M}C_1.$$

Thus,

$$W' = \frac{mC_1^2}{2}\left(1 + \frac{m}{M}\right)$$

$$= \frac{m + M}{M}W_r.$$

Accordingly,

$$\frac{1}{2}m(u^2 - U^2) = \frac{m + M}{M}W_r.$$

The law of conservation of moment of momentum furthermore requires that $ru = bU$, for b is the radius of rotation about M when the velocity is U, and r is that when the velocity is u. Thus

$$r^2 = b^2\left(\frac{U}{u}\right)^2,$$

and, as

$$u^2 = 2\frac{m + M}{mM}W_r + U^2,$$

then

$$r^2 = b^2\left(\frac{U^2}{2\dfrac{M + m}{mM}W_r + U^2}\right)$$

$$= b^2\left(1 + \frac{2W_r}{\dfrac{mM}{m + M}U^2}\right)^{-1}.$$

Now the condition for a collision is that s, the sum of radii of ion and molecule, should be equal to or greater than r. Thus for a collision, s^2 must be such that

$$s^2 \geq b^2\left(1 + \frac{2W_s}{\frac{mM}{m+M}U^2}\right)^{-1},$$

that is, for impact, the square of the perpendicular from the molecule on the initial direction of motion of the ion must be equal to or less than the square of the original sum of radii of ion and molecule multiplied by the factor

$$\left(1 + \frac{2W_s}{\frac{mM}{M+m}U^2}\right) \quad \text{or} \quad b^2 \leq s^2\left(1 + \frac{2W_s}{\frac{mM}{M+m}U^2}\right).$$

Thus, with no forces acting, collision occurs when $b \leq s$. With forces, b^2 can be equal to or less than s^2 multiplied by a factor greater than unity by the ratio $\dfrac{W_s}{\frac{1}{2}\frac{mM}{M+m}U^2}$, to be defined later.

Thus the s_f, when forces of the form above act, is related to the s when no forces act by the equation

$$s_f^2 = s^2 + \frac{2s^2W_s}{\frac{mM}{M+m}U^2}.$$

Now

$$\frac{1}{2}mU^2 = \frac{1}{2}mC_1^2\left(1 + \frac{m}{M}\right),$$

$$U^2 = C_1^2\left(1 + \frac{m}{M}\right),$$

$$\left(\frac{MU^2}{m+M}\right)\frac{m}{2} = \frac{mC_1^2}{2} = \frac{MC^2}{2},$$

where $MC^2/2$ is the kinetic energy of agitation of the gas molecules. Thus $s_f^2 = s^2\left(1 + \dfrac{2W_s}{MC^2}\right)$. The s^2 in Langevin's λ is, accordingly, to be replaced when forces act by s_f^2, so that Langevin's equation becomes, for this case,

$$k = 0.815\frac{e}{M}\frac{\lambda}{\left(1 + \frac{2W_s}{MC^2}\right)C}\sqrt{\frac{m + M}{m}},$$

the value of k thus being merely divided by the quantity $\left(1 + \frac{2W_s}{MC^2}\right)$. This is unity plus the ratio of the potential energy of ion and molecule at impact to the kinetic energy of thermal agitation. Substituting for W_s, this becomes

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\frac{\sqrt{\frac{M + m}{m}}}{\left\{1 + \frac{(D - 1)e^2}{4\pi NMC^2s^4}\right\}}.$$

Now it was found that the ratio of potential to kinetic energies for a molecular ion in contact with a molecule (*i.e.*, for a small ion at impact) was 3.1. Thus, the Wellisch factor reduces k from the value 11.7 calculated for a forceless ion to 11.7/4.1 = 2.86 cm/sec. per volt/cm. This value is in fairly good agreement in order of magnitude with the observed value. The criticisms of this theory lie in the application of the factor $2W_s/MC^2$ as calculated above to a small-ion theory, for the value of this factor, as shown before, suggests a cluster formation. Another minor weakness of this theory is that it neglects the loss of momentum of the ion gained in the field in cases where its path is curved, and it thus exchanges momentum with the molecule but does not actually collide. The amount of error introduced by this neglect is of the order of 10 per cent, as a rigorous calculation by J. J. Thomson shows.[28,29] The change in k by such a correction would be less than 10 per cent, and the k above would become 2.6 cm/sec. per volt/cm. The theory is interesting, however, in that it shows that the forces will, with an elastic-impact theory, yield a value of the mobility which is in fair agreement with experiment. It is to be noted in passing that the mobility is a function of the charge e of the ion in both this and the Langevin equation. It is, however, less so than appears on the surface, for, if the ion cluster depends on the value of e, or if the attractive forces do, they will bring in e to increase s^2 and thus introduce a factor dependent on e in the denominator.

106. Other Equations for the Mobility of Ions and the Nature of the Ion.—In the first edition of this text an equation of J. J. Thomson[28] was deduced on the basis of the energy lost by an

ion which attracted molecules with an inverse fifth power law of force, taking into account the momentum exchange between ions and molecules which did not collide as well as those which did collide. In his deduction Thomson made an assumption open to question. He assumed that the ion was a mass-point center of force and that when it "collided" with the surface of a molecule it merely reversed its direction and retraced its path. This could never happen for a real ion and a molecule, as both have finite size, and in an encounter the surfaces in contact would determine the nature of the paths after impact. Langevin,[31] in his classical derivation of the expression for the mobility of a spherical ion in a gas composed of spherical molecules attracted to the ion by the inverse fifth power law to be discussed later, was required to meet the same problem. He, however, approximated the average change of path on spherical impacts of bodies moving in inverse-fifth-law orbits. His solution, while thus approximate to some extent, is superior to the solution obtained by Thomson. In 1924 Loeb,[29] in ignorance of Langevin's classical study of 19 years before, applied Thomson's equation to the evaluation of the ionic mobility. This led to a most interesting equation for the mobility in that it showed the nature of the real mobility problem from the theoretical point of view. It later appeared that Langevin had much earlier obtained an equation identical with Loeb's, except for the value of the constant factor, as the special case of his general equation for which the ionic radius becomes vanishingly small. It is probable that the constant in Langevin's equation is more accurate than that of Loeb, since Langevin properly treated the reflection of the ions from the spherical molecules. The equations obtained are as follows:

Thomson-Loeb[29] $$k = \frac{0.104\sqrt{\frac{M+m}{m}}}{\frac{\rho}{\rho_0}\sqrt{(D-1)_0 M_0}}.$$

Langevin[31] $$k = \frac{0.235\sqrt{\frac{M+m}{m}}}{\frac{\rho}{\rho_0}\sqrt{(D-1)_0 M_0}}.$$

Actually Langevin writes his equation $k = \frac{0.505\sqrt{\frac{M+m}{m}}}{\sqrt{\rho(D-1)}}.$

Here ρ is the density of the gas $= nM$, where n is the number of molecules per cm^3. As $n = \frac{\rho}{\rho_0} N_0$, where ρ_0 is the density at 0°, 760 mm, and N_0 is the Loschmidt number, and as $(D - 1) = \frac{\rho}{\rho_0}(D - 1)_0$ where $(D - 1)_0$ is the dielectric constant at 0°, 760 mm, and since $M = M_0\mu$ where μ is the mass of the H atom and M_0 the atomic weight, one can derive the expressions given above by putting in the value for the constants μ and N_0.

These equations are of importance in that they give the mobility of the ion with no arbitrary assumptions as to its size and based entirely on the inverse-fifth-power-law attraction, showing that attractive forces without a cluster can account for the mobility. They represent in a sense the true small-ion type of action in an extreme form. In these equations the factor $\sqrt{\frac{M + m}{m}}$ is the mass factor common to all but Lenard's mobility equation.[21,26] It is seen that it does bring in the assumption of the ion size through the value of m/M. In this case, however, the factor plays a minor rôle in the fivefold lowering of the mobility, for the $\sqrt{\frac{M + m}{m}}$ changes its value from 1.41 to 1 in the extreme range from $m = M$ to $m = \infty$. If m were less than M, the effect would be striking. Unfortunately it was in the past not possible completely to test this point, due to the fact that in early experiments in H_2 and other gases m was never known for the ions studied.[30,71] The reason is that no matter what atom or molecule may have been ionized, unless its ionization potential was less than that of the gas molecules in which it moved, the ion changed its charge, and, in any even slightly impure gas such as those used, it picked up another molecule to change m.[81] However, in the recent experiments of Tyndall and Powell[78] and Powell and Brata,[79] using unaged ions of the alkali atoms Li^+, Na^+, K^+, etc., in He, Ne, Ar, Kr, etc., the law has very recently been put to an adequate test in this regard. It appears that the mass factor is adequate to give the observed results under conditions where the equation above applies. As regards the other quantities, they are well known and contain no implications about the ion. The ratio ρ/ρ_0 is the density of the gas when k is measured, relative to the density under standard conditions of 0°C. and a pressure

of 1 atm. The quantity D is the dielectric constant of the gas in bulk and the expression $(D-1)_0$ means that D is determined under conditions for which ρ_0 is determined. M_0 is the molecular weight of the gas.

Since the assumptions involve point charges, it is clear that radii play no rôle and the deflections are produced by the force fields alone. In general this does not correspond to reality. According to Tyndall and Powell,[78] however, in a number of the inert gases, D is great enough so that the forces causing momentum loss for the motion of the ions in the field are largely those due to the dielectric attractions, and thus the elastic solid collisions involving physical radii should play a minor rôle. Under these conditions the law might be obeyed with fair precision, and the mobility should be given by the equation which they give in Langevin's form as

$$k = \frac{A\sqrt{\frac{M+m}{m}}}{\sqrt{\rho(D-1)}}.$$

In their equation, A is a function of s, the closest approach of ion and molecule in collision (*i.e.*, the sum of the elastic solid radii of ion and molecule), the dielectric forces, and the gas temperature (*i.e.*, of $D-1$). For the case where the solid elastic radii do not play an important rôle (*i.e.*, for larger values of $D-1$), these investigators find the equation to hold quite well. Langevin's theory gives $A = 0.51$ as used by them, while the observed values are $A = 0.54$ for Ar, $A = 0.55$ for Kr, and $A = 0.56$ for Xe. Figure 72 shows the results for the mobility of the various ions as a function of the mass of the ion in Ar, curve 1, and in He, curve 2. The full lines are the ratio of the mobilities of other ions relative to Na^+, assuming the law given above to hold. The points are the observed ratios. It is seen that in Ar the observed and predicted values agree very well, while in He, where $(D-1)$ is small, the ions K^+, Rb^+, and Cs^+ depart quite widely. It is interesting to note in addition that the equation gives not only the correct order of magnitude but very nearly the true values of the mobilities in cases where the nature of the ion is definitely known. This, in fact, might have been expected once experimental values of the mobility of such nature as to have theoretical significance had been obtained in the laboratory, for already in 1924 Loeb[29] had shown

that the equation he had derived from Thomson's theory gave not only the right order of magnitude of the mobility for most gases but gave the relative values for the different gases in nearly the order observed. The departures observed were all of the nature of the differences in mobilities of positive and negative ions which have since been shown to be largely governed by complex ion formation. Loeb,[77] and later Powell and Brata,[79] have observed the formation of complexes with age for alkali ions in different gases. Powell and Brata remark that the complex ion formation exerts relatively little influence on the mobilities. It is thus clearly brought out by this theory, as Loeb had long ago pointed out, that *the major portion of the fivefold lowering of the mean free path of gaseous ions was due to that action of the dielectric attractive forces which did not produce a clustering;*[29,30] while complex ion formation,[69,71,76] a form of clustering, does produce changes of a minor order.

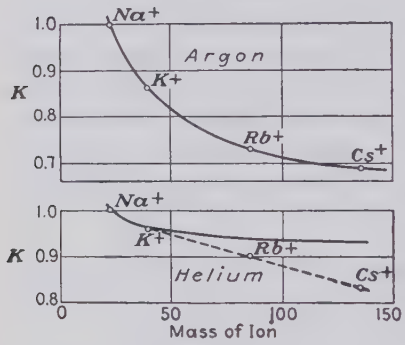

FIG. 72.

The simplified mobility equation also has other advantages in that it accounts for the observed features of the ionic mobilities. It is seen that the value of k is independent of field strength according to this equation, as in all mobility equations. This has been observed to be the case up to fields which are about half that for sparking in the gas.[82] This incidentally also indicates that the ion complexes are quite stable and do not show the easy disintegration on impact to be expected of large clusters. The independence of mobility and field strength should hold until the paths of the ions are curved materially in the field so that the Langevin equation no longer holds. It is seen that on the theory above, k is proportional to ρ_0/ρ which is observed to be the case over a considerable range of densities, namely, from that at some 60 atm. pressure to less than a mm of pressure, temperature remaining constant. If density is constant, it is seen that k should be independent of temperature. This is surprising, as the simple solid elastic theory of Langevin,

$$k = 0.815\frac{e}{M}\frac{\lambda}{C}\sqrt{\frac{m+M}{m}},$$

requires k to be proportional to $1/C$ or to $T^{-\frac{1}{2}}$. The cause for this independence in the dielectric theory lies in the fact that increases in T, while increasing random heat motion and thus decreasing k, also decrease the influence of the attractive forces of ions for molecules in the same measure. A partial action of this type is seen best in Wellisch's equation where, if forces play a great rôle, and $PE/\frac{1}{2}MC^2 >> 1$, the C on the outside of the parenthesis in part cancels the $1/C^2$ inside. On the full Langevin theory there would be a small temperature variation as is the case in Wellisch's theory. While the data on the temperature coefficient of the mobilities are quite conflicting,[38,39] it can be said that the very careful experiments of Erikson[10] showed k to be independent of T down to nearly liquid-air temperatures, and at those temperatures the decrease was only 10 per cent, which might have been explained in some other fashion. Modern data for k over a significant temperature range unfortunately do not exist. Finally it is observed that k is independent of the charge on the ion according to this theory. This follows from the fact that, while the force on the ion is proportional to the charge, the frictional drag due to the dielectric constant is also proportional to the charge. Hence the charge cancels out. This was already noted in the case of Wellisch's theory. Actually the problem never arises in practice, despite beliefs to the contrary,[13] for multiply-charged ions are only infrequently generated and the work of Kallmann and Rosen[72,81] on exchange of charges shows that, with the many impacts of a multiply-charged ion with neutral molecules during a study of its mobility, the ion will quickly lose its multiple charge and the mobility will depend largely on the single charge.

The variation of k with $\sqrt{M_0}$ had long ago empirically been observed by Kaufmann,[17] and Loeb[32] as early as 1917 showed that k varied as some power of $1/(D-1)$. This, together with the successful calculation of mobilities for different ions, establishes the viewpoint on which the equation is based as relatively proper.

Hence one may conclude that, while in general this simple form of equation is not accurately applicable to the problem, it can be applied with some success in the case of gases with a

high dielectric constant. The equation is, however, very valuable in that it shows that a large cluster ion is not essential for an explanation of the values of ionic mobilities. Taken in connection with the work on mixtures[71] and aging,[13,69] as well as mass spectrograph[80] studies, it helps to a clear understanding of the nature of the ion.

Before proceeding to discuss in detail the more accurate theory of Langevin as modified by Hassé,[40] it is of importance to discuss briefly the mobilities of ions in gaseous mixtures. At the time the intensive study of anomalous gases which eventually led to the understanding of the differences of the mobilities of the positive and negative ions was begun, Loeb[29] had just derived his version of the Langevin equation from Thomson's theory. Considerations based on this theory, in the absence of the very recent data on the freshly formed alkali ions of known nature in gases, led Loeb[36] to the conclusion that the behavior of the ions in pure gases could never clearly differentiate between the small-ion and cluster theories. In a more picturesque fashion of speaking, this was equivalent to saying that in pure gases the behavior of the ion indicated the "ignorance" of the ion as to whether it was a cluster or a single charged molecule. A study of mobilities in mixtures of radically different gases whose D varied widely seemed, however, to promise a definite answer. If an ion in a gas a has a mobility k_a and in a gas b the ion has a mobility k_b, and if the nature of the ion is the same in both gases such that it is unchanged on mixing the gases, one can predict its mobility in a mixture of the two gases in any proportions quite easily. This must follow if the nature of the ion is unchanged in that the only effect of the mixed gases on the mobility will be for each gas to contribute its influence on the ion in retarding it in proportion to its partial pressure. To understand this, one may follow the reasoning of Blanc,[35] who in 1908 derived and proved the law on mixtures of H_2, air, and CO_2. Consider R, the resistances of the gases to the motion of the ions, the resistance being R_a in the gas a and R_b in the gas b. Now the resistance a gas offers to an ion will be inversely proportional to the mobility. Hence one can set $R_a = d/k_a$, and $R_b = d/k_b$, where d is constant. Then, if there is a fraction of the pressure f_a due to molecules of gas a in the binary mixture, the fraction of the pressure due to molecules of gas b will be $1 - f_a$. Accordingly the total resistance

of the gas, R_f, will be merely the sum of the product of the resistance R_a of the gas a times the fraction of the pressure which it causes and R_b times its fractional pressure. Thus,

$$R_f = f_a R_a + (1 - f_a)R_b$$
$$= \frac{f_a d}{k_a} + \frac{(1 - f_a)d}{k_b} = \frac{k_b f_a d + k_a(1 - f_a)d}{k_a k_b},$$

and, since one can write that the mobility in the mixture $k_f = d/R_f$, k_f is given by

$$k_f = \frac{k_a k_b}{f_a k_b + (1 - f_a)k_a}.$$

It had been believed by some that in water vapor and other gases this law was not obeyed,[32] although in 1924 no systematic quantitative deviation had been observed. If the law is not obeyed, then it means that, in some way, either the ion is altered on mixing or else the ion by its presence alters the mixture in some fashion. Extensive investigations first by Loeb and his students, and later by Tyndall and his students, and by Mayer, over a number of years, showed that, in fact, two types of action occurred.[72,76] The most striking effect was that observed on mixing NH_3 and H_2, ether and H_2, and Cl_2 and H_2. It was observed that in the first two cases the minutest traces of the gases NH_3 and ether produced sudden changes in the mobility of the positive ions, NH_3 increasing the mobility, while ether reduced the mobility. The negative ion in ether was unaffected, but in NH_3 a small deviation of a different nature from the Blanc law curve was observed. The negative ion had its mobility abruptly lowered for mere traces of Cl_2 in the H_2, while the positive ion was unaffected. The interpretation is simple. NH_3 adds to the positive ion, replacing some bulkier molecule attached to the charged molecule and thus decreasing the radius and increasing the mean free path of the ion as usually observed in the none-too-pure H_2. In the case of ether, the very bulky ether molecule was selectively picked up by the ions in preference to the less bulky natural impurity present, increasing the size of the ions and reducing their free path. While both CH_3NH_2 and $CH_3CH_2CH_2NH_2$ add to the positive ion in H_2, CH_3NH_2 unlike NH_3 leaves the ion mobility unchanged, indicating that the size of the CH_3NH_2 addition product is the same as the impurity on the normal ion in the H_2. $CH_3CH_2CH_2NH_2$,

on the other hand, adds and sharply lowers the positive mobility because it forms a much bulkier complex. Analogous results were obtained by Tyndall and Grindley on the negative ions with the alcohols. Even then the change in mobility produced by very bulky molecules is not a very profound change, although the size of the ion may be very much increased. This again bears out the evidence from the experiments of Powell and Brata in the inert gases that the solid elastic radius plays a minor rôle in determining the value of the mobility.

On the other hand, in very polar gases, such as NH_3 and HCl, Loeb observed that there was on the less affected ion (negative in NH_3, positive in HCl) a departure from the Blanc law of a different sort. It was a gradual departure towards a lowered mobility in the intermediate ranges of composition becoming negligible again at high concentrations of either constituent. Debye interpreted this phenomenon as being due to the effect of the field of the ion in changing the composition of the gas in its immediate neighborhood, due to dielectric attraction. Thus the ion like the proverbial "Flying Dutchman" always travels in a mist of the more active molecules. In a sense this is a cluster, but at best it is only a statistical one and one which is exceedingly labile, constantly changing and easily destroyed. The quantitative value of this effect can only be roughly included in the Blanc law. Condon proved that such an effect must occur and, by the reasoning outlined, laid the foundation for the rough investigation of this effect. It is, in fact, analogous to the change in density due to forces which give the temperature variation in Van der Waals' a (see page 146). Condon calculated the change in concentration of HCl gas in an HCl-air mixture as a function of the distance from the ion due to the dielectric attraction of the ion for the HCl molecule.

In Chap. VIII it was shown that in the earth's gravitational potential field the number of molecules per cm^3 varied with the altitude above the surface according to the relation $n = n_0 e^{-\left(\frac{Mg}{R_A T}\right)h}$. There is, however, nothing in the derivation of this law to prevent its being applied to the case of any attracting force field as long as the conditions governing the application are fulfilled, and the law actually follows directly as a consequence of equipartition as indicated on page 95. One can, for simplicity, divide M and R_A by N_A, the Avogadro number, thus giving m, the molecular mass, and k, the Boltzmann constant.

Then the gravitational potential mgh is equivalent to the potential energy U of the ion in the field of force. Thus in a more general form, one can write $n = n_0 e^{-\frac{U}{kT}}$, where n_0 is the number at some chosen reference plane and U is the potential-energy difference between that plane and the plane n where the count n is being taken. Now the ion is surrounded by a field of force and hence at each point in the field a molecule of moment μ, yielding a gas of dielectric constant D, has a potential energy given by

$$U = \frac{-(D-1)e^2}{8\pi N_0 r^4} = -\frac{\mu e}{2r^2}.$$

Thus in the potential field of an ion there must be a distribution of molecules according to the law

$$n = n_0 e^{+\frac{(D-1)e^2}{8\pi N_0 r^4 kT}}.$$

Here r is the distance from the center of the ion and, as the exponential term is unity for r infinite, $n = n_0$ is the number of molecules at infinity, *i.e.*, where the force field ceases to attract the molecules appreciably. n is the number at any distance r less than infinity. Actually for practical purposes at $r = 10^{-5}$ cm, with the dielectric forces usually found, $n = n_0$, while, at 10^{-8} cm, $n >> n_0$. It is seen that the density of ions due to the force field will fall off very rapidly as r increases. Now consider a gas composed of a mixture of molecules of types a and b having widely different dielectric constants D_a and D_b. One can at once write that the distribution of the concentrations of molecules a and b, N_a and N_b, at a distance r from the ion will be given by the relations

$$N_a = N_{a0} e^{+\frac{(D_A-1)e^2}{8\pi N_0 r^4 kT}},$$
$$N_b = N_{b0} e^{+\frac{(D_B-1)e^2}{8\pi N_0 r^4 kT}},$$

where N_{a0} and N_{b0} are the numbers of molecules a and b per unit volume originally in the mixture and infinitely far removed from the ions. Thus at a distance r the relative number of molecules of types a and b will be given as

$$\frac{N_a}{N_b} = \frac{N_{a0}}{N_{b0}} e^{+\frac{[(D_a-1)-(D_b-1)]e^2}{8\pi N_0 r^4 kT}}$$
$$= \frac{N_{a0}}{N_{b0}} e^{\frac{(D_a-D_b)e^2}{8\pi N_0 r^4 kT}}.$$

It is thus seen that, if D_a is greater than D_b, N_a/N_b will be greater than N_{a0}/N_{b0}, the original ratio of concentrations in the mixture, by a factor which varies as $e^{(D_a-D_b)/r^4T}$, *i.e.*, which varies with the difference in dielectric constants and the fourth power of the distance. The difference in $D_a - D_b$ can be considerable, and this factor can also vary over an appreciable range so that there is a real difference in concentration of the two species about the ion for different combinations of gases. An idea of the effect of the Condon relation can be gained by substituting the values for D_a and D_b for HCl and air into the equation, assuming T as 273° abs. and $N_0 = 2.7 \times 10^{19}$. The relation then yields

$$\frac{N_a}{N_b} = \frac{N_{a0}}{N_{b0}} e^{\frac{2.83\times10^{-29}}{r^4}} = f_{a0}e^{\frac{2.83\times10^{-29}}{r^4}}$$

Values of $\frac{N_a/N_b}{f_{a0}}$ for various values of r are given in the table below.

r IN CM $\times 10^8$	$\frac{N_a/N_b}{f_{ab}}$
1.14	10^{700}
4.0	545
5.74	13.5
6.9	3.4
8.0	2.34
9.2	1.48
11.4	1.17
13.8	1.08
114.0	1.000016
1140.0	1.00000000

The effect on the Blanc law is somewhat difficult to establish as will be seen. In Blanc's law the mobility

$$k_f = \frac{k_a k_b}{f_a k_b + (1 - f_a)k_a},$$

where a and b correspond to the gases a and b above. For a gas where the relative concentration is unaffected by the forces, f_a is the same as f_{a0}. If, however, the concentration effect is present, f_a in the equation cannot be set equal to f_{a0} but is really $f_{a\bar{r}} = \frac{N_a}{N_b} = f_{a0}e^{\frac{(D_a-D_b)e^2}{8N_0\pi\bar{r}^4kT}} = f_{a0}e^{G/\bar{r}^4}$, where the bar represents an average value and

$$G = \frac{(D_a - D_b)e^2}{8\pi N_0 kT}.$$

Now it is difficult to fix the average value, for the average value strictly would be represented by

$$f_{a\bar{r}} = \frac{f_{a0}\int_{\sigma}^{\infty} e^{\frac{G}{r^4}}\, dr}{\int_{\sigma}^{\infty} dr} = 0,$$

σ being the sum of the radii of ion and molecule. Actually for very large distances from the ion the concentration change is not important as regards the mobility. In fact the concentration will act on the mobility only through its effect on the free path. Hence it is possible in a rough calculation to restrict the concentration change to *an average value* lying between the diameter σ and L the free path. Accordingly the proper procedure for an approximate study would be to replace the f_a in Blanc's law by

$$f_{a\bar{r}} = f_{a0}\frac{\int_{\sigma}^{L} e^{\frac{G}{r^4}}\, dr}{\int_{\sigma}^{L} dr}.$$

An evaluation of this quantity for an HCl and air mixture was kindly carried out by R. N. Varney and yields the value of f_a between the values $\sigma = 4.00 \times 10^{-8}$ cm and $L = 6.86 \times 10^{-6}$ cm, as $f_{a\bar{r}} = 10.17 f_{a0}$. The resultant effect on $R_f = 1/k_f$ will be to cause R_f, instead of following a linear course from $f_a = 0$ to $f_a = 1$, to follow a linear course with a slope increased by the factor $f_{a\bar{r}}/f_{a0}$ from $f_{a\bar{r}} = 0$ to $f_{ar} = 1$, after which R is constant. The actual curves for R_f show this character, the ratio $f_{a\bar{r}}/f_{a0}$, however, being small and the transition at $f_{a\bar{r}} = 1$ more gradual than the rough theory requires, as might be expected.

The problem of an accurate theory of ionic mobility using the inverse fifth power law of attractive force, assuming solid elastic impacts, was attacked from a classical kinetic-theory point of view first by Langevin[31] in 1905. Instead of the simple mean-free-path concept in his approach to the problem, Langevin used the more general method of approach initiated by Maxwell and later developed by Boltzmann for the study of transfer problems. By this means the expression for the coefficient of diffusion of the ions was developed and applied to the study of mobilities. The method is well beyond the scope of

this text and will not be given. Under the inverse fifth power law of attraction the orbits of the ion and the molecule must be computed. The effects of these orbits on the energy and momentum exchange must be accounted for and evaluated. Since in some cases the orbits lead to deflection without impact, and in others the orbits lead to impacts between the assumed elastic spherical ions and molecules, the considerations are quite complex. A solution of the problem led Langevin to an equation for the mobility of the form

$$k = \frac{3}{16Y}\frac{1}{\sqrt{(D-1)\rho}}\sqrt{\frac{M+m}{m}},$$

where Y is a function of a constant μ given by $\mu^2 = \frac{(D-1)e^2}{8\pi p\sigma^4}$, σ being the sum of the radii of ion and molecule and p the gaseous pressure. The relation between $\frac{3}{16}Y$ and $1/\mu$ is shown in

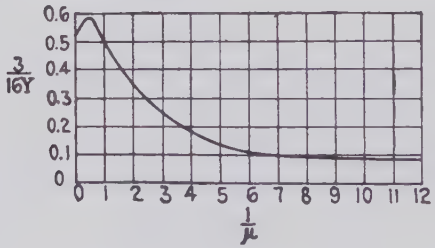

FIG. 73.

Fig. 73. It is seen to have a maximum at $1/\mu$ about 0.5. The curve, were no attractive forces present, would follow an asymptotic curve, coincident with the one plotted, from $1/\mu = 12$ to $1/\mu = 3$, which thereafter increases rapidly to a point giving $\frac{3}{16}Y = 0.9$ at $1/\mu$ of about 0.8. The equation expressed in Loeb's notation is

$$k = \frac{3}{16Y}\frac{0.465\sqrt{\frac{M+m}{m}}}{\frac{\rho}{\rho_0}\sqrt{(D-1)_0 M_0}}.$$

For the case of $1/\mu = 0$, as stated before, the quantity $\frac{3}{16}Y$ in Langevin's form becomes 0.505 and in the equation above, 0.235 (see page 565).

In 1926 Hassé[40] made a critical study of Langevin's equation. In this study he recalculated the integrals dealing with the

different types of orbits given by Langevin. He expresses Langevin's theory as

$$k = \frac{A}{\sqrt{\rho(D-1)}}\sqrt{\frac{m+M}{m}},$$

where A is again a function of a quantity λ defined by $\lambda^2 = \frac{8\pi p\sigma^4}{(D-1)e^2}$. The function as recalculated by Hassé is best given in the form of a table from $1/\mu = 0$ to $1/\mu = 4$.

λ	A	$A\lambda$	λ	A	$A\lambda$
0.0	0.5105	0.0000	2.1	0.3370	0.7077
0.1	0.5488	0.0549	2.2	0.3236	0.7119
0.2	0.5648	0.1130	2.3	0.3111	0.7155
0.3	0.5756	0.1727	2.4	0.2994	0.7186
0.4	0.5836	0.2334	2.5	0.2886	0.7215
0.5	0.5886	0.2943	2.6	0.2784	0.7238
0.6	0.5904	0.3542	2.7	0.2689	0.7260
0.7	0.5878	0.4115	2.8	0.2599	0.7277
0.8	0.5796	0.4637	2.9	0.2515	0.7293
0.9	0.5662	0.5096	3.0	0.2436	0.7308
1.0	0.5483	0.5483	3.1	0.2362	0.7322
1.1	0.5277	0.5805	3.2	0.2292	0.7334
1.2	0.5057	0.6068	3.3	0.2226	0.7346
1.3	0.4834	0.6284	3.4	0.2163	0.7354
1.4	0.4614	0.6460	3.5	0.2104	0.7364
1.5	0.4402	0.6603	3.6	0.2048	0.7373
1.6	0.4201	0.6722	3.7	0.1994	0.7378
1.7	0.4011	0.6819	3.8	0.1944	0.7387
1.8	0.3834	0.6901	3.9	0.1895	0.7391
1.9	0.3668	0.6969	4.0	0.1849	0.7396
2.0	0.3514	0.7028			

The values lie close to Langevin's and at $\lambda = 0$, $A = 0.5105$. In Hassé's discussion of the use of the equation for computing mobilities it is clear that ρ, D, and M can all be accurately evaluated. On the other hand, the value of m is uncertain except in the case of alkali ions in inert gases before complex ion formation can take place. The real difficulty lies in the value of σ, the sum of the radii of the ion, s and the molecule, S required to evaluate λ. In general, while S could be taken from the kinetic theory for the molecules, s is not known unless the ion is monomolecular when its value could be guessed from atomic-

structure data. If the ion is a complex, the value of s would merely be a conjecture.

In addition the problem is complicated by the fact that these radii are determined by the attractive and repulsive force fields of the atom and the ion. If it could be assumed that the *charge on the ion did not alter the attractive or Van der Waals forces,* then the attractive inverse-fifth-power dielectric force would have to add to the attractive Van der Waals force and the repulsive force between molecule and ion would have to be taken into account. Actually, to the author it is unthinkable that in the intense inverse-fifth-power-law field, due to the charge on the ion, the Van der Waals *attractive* force between the uncharged carrier and molecule should not be completely altered. It is also probable that the *repulsive* force between ion and molecule would be altered but probably not in the same measure as is the attractive force. In general, however, the Van der Waals attractive forces are negligible compared with the dielectric forces and can easily be ignored. The repulsive forces, while changed, vary so rapidly with distance that these can be considered relatively the same. Actually in the first study of Hassé the law as deduced did not allow for the forces directly but only called for a radius defined by such forces. Hassé then assumed that the dielectric forces acted independently and took the radius σ for ion and molecule from the values for uncharged molecules from Jeans' evaluation of S from the coefficient of viscosity, or computed an S from observations on the Van der Waals forces inferred from viscosity. In this case σ gives the diameter for neutral molecules, taking into account attractive and repulsive forces. The values obtained by Hassé, assuming *monomolecular* ions, were somewhat high compared to the observed values. Computations of the mobility for a monomolecular layer cluster about a charged positive molecule as the positive ion and a similar cluster about an *electron* as the negative ion gave a fair agreement between observed mobilities for positive and negative ions and Hassé's theory. Actually the type of negative cluster assumed by Hassé cannot form, as the electron would first be incorporated into a molecule and would thus form a cluster similar to a positive ion. It is of interest to see how little the mobility values are altered by large changes in m and σ on this theory. Actually the above agreement on the cluster theory is accidental, as has

since been shown. The so-called normal values of the mobilities observed for ions in relatively pure gases at ages of more than 10^{-3} sec. used for comparison above, while important constants for the calculations of currents, are absolutely meaningless in terms of any ion theory. No matter what the originally charged molecule of an ion in a gas, such as those used above, is, there is no telling what the charged molecule is at the time of measurement, in view of the ready changes of charge observed by Kallmann and Rosen.[81] In addition, the large cluster composed of molecules of the gas present does not form and, as the mixture work shows, will never form, if there are present even chemically undetectable traces of some more active gas. Hence ordinary ions, having made some 10^6 impacts at the time of measurement, are unknown quantities. In the case of Loeb's[77] experiments using alkali ions in short time intervals, *e.g.*, 10^{-5} sec., and especially in the later experiments of Tyndall and Powell,[78] and Powell and Brata,[79] using the same conditions with their exceptionally fine measuring device, the values of the mobilities observed have theoretical significance for the first time. In these measurements the agreements between theory and experiment are exceedingly good and in fact perhaps better than might be expected.

In a later article Hassé and Cook[33] use the methods of their very pretty analysis of the coefficient of viscosity, assuming molecules which attract according to an inverse fifth power law and repel according to an inverse ninth power law, for the calculation of ionic mobilities of monomolecular ions. The forces assumed are the attractive forces between molecules of the form μr^{-5} and repulsive forces of the form λr^{-9} already discussed in Sec. 64. The calculation was based on theoretical considerations prior to the advent of the new quantum mechanics. This viewpoint is characterized by two assumptions: the first is the existence of the classical electrical attractive force between the ion and molecule of the form

$$\frac{(D-1)e^2}{2\pi N r^5} = qr^{-5},$$

and the second is that this electrical attractive force and the Van der Waals attractive force μr^{-5} have their constants merely add, while both the μr^{-5} and λr^{-9} forces *remain unaltered.* While perhaps the addition of the constants μ and q is to be questioned, and the use of a law of the form r^{-9} instead of the more nearly

correct e^{-br} law of the quantum mechanics might be questioned, the results deserve being given as probably the best results to be obtained on classical theory. With the complexity of the wave-mechanical solution and the small hope of its speedy application, they will doubtless represent the best results to be had for some time. The course of the calculation follows closely the outline in their article on viscosity and is beyond the scope of this text. The equation resulting is given by

$$k = \frac{3}{16}\frac{e}{2\sqrt{\pi}RT}\left[\left(\frac{M+m}{Mm}\right)2RT\right]^{\frac{3}{4}}\frac{(1+\epsilon)}{N_0 I(s)(\lambda')^{\frac{1}{4}}}$$

which for a monomolecular ion, where $M = m$, gives

$$k = \frac{3e}{16}\left(\frac{2}{\pi M}\right)^{\frac{1}{2}}\frac{1}{(2RT\lambda)^{\frac{1}{4}}}\frac{(1+\epsilon)}{N_0 I(s)}.$$

In this expression $\lambda' = \lambda\dfrac{M+m}{Mm}$, λ is the coefficient of the repulsive law of force, $s^2 = \dfrac{2RT\lambda}{{\mu_1}^2}$, where μ_1 is the coefficient of the combined Van der Waals and electrical attractive forces (*e.g.*, as assumed by Hassé and Cook $\mu_1 = \mu + q$), and $1 \pm \epsilon$ is a correc-

s	$I(s)$	s	$I(s)$
0.05	2.2584	1.1	0.2866
0.10	1.5619	1.2	0.2848
0.15	1.2496	1.3	0.2839
0.20	1.0431	1.4	0.2836
0.25	0.8634	1.5	0.2836
0.30	0.7129	1.6	0.2838
0.35	0.5971	1.7	0.2842
0.40	0.5121	1.8	0.2846
0.45	0.4508	1.9	0.2852
0.50	0.4067	2.0	0.2857
0.55	0.3747	2.2	0.2867
0.60	0.3515	2.4	0.2878
0.65	0.3343	2.6	0.2888
0.70	0.3216	2.8	0.2897
0.75	0.3121	3.0	0.2905
0.80	0.3049	3.2	0.2913
0.85	0.2995	3.4	0.2920
0.90	0.2953	3.6	0.2927
0.95	0.2922	3.8	0.2933
1.00	0.2898	4.0	0.2938

tion factor which for elastic spheres, according to Chapman, lies between 1 and 1.015. The quantity $I(s)$ is an integral which is given for various values of s in the table on page 580.

For the calculation of k in H_2, $\lambda = 0.106 \times 10^{-72}$ and the μ due to molecular attractions is $\mu = 0.35 \times 10^{-43}$. The q due to the dielectric attraction is given by $q = 3.54 \times 10^{-43}$, and the μ_1 above is taken as $\mu_1 = \mu + q$. This gives $s = 0.235$ and $I(s) = 0.897$. The mobility computed at 15°C. and 760 mm is 18.3 cm/sec.

The various values calculated on this theory and on other theories are given below.

MOBILITY OF MONOMOLECULAR IONS

Gas	Elastic sphere	Sutherland model	Centers of force	Observed
Air	3.41	3.13	3.35 [a]	
Argon	2.95	2.68	2.68 [a] 3.13 [b]	2.78
Helium	26.3	24.9	29.9 [b]	21.4
Nitrogen	3.44	3.17	3.47 [a] 4.05 [b]	3.04 [c]
Hydrogen	19.0	18.2	18.3 [a] and [b]	13.3

[a] Data obtained from viscosity.
[b] Data obtained from equation of state.
[c] Value is that of Powell and Brata. Loeb found 3.75 and 17.5 for Na^+ ions in N_2 and H_2 respectively.

In the first column are given values for the Langevin theory, using the values of the radii from viscosity. In column 2 a model due to Sutherland is used in which a basic radius s_0 is assumed due to the repulsive force. The Van der Waals attractive force is then added to the electrical attractive force, and the mobility is deduced on the Langevin theory with a different value of the attractive force constant. The third column gives the calculation, assuming centers of force as above. There are also included the observed values of Tyndall and Powell for combinations that are nearest to the true conditions; they are He^+ in He, K^+ in Ar, Li^+ in H_2. The agreement is fairly close in all cases. It is seen that the values found are very little changed on the various theories. This indicates that with the inadequate data at hand, both as to real values of the mobilities and as to the constants, refinements in the theory have relatively little new to offer for the present.

In conclusion, Powell and Brata's[79] table of values of the mobilities of ions of a known nature in pure gases taken in such short time intervals that they have not attached is given below.

OBSERVED MOBILITIES OF MONOMOLECULAR IONS

Gas	Li^+	Na^+	K^+	Rb^+	Cs^+
He	25.3	23.2	22.4	21.0	19.0
Ne	14.35	9.00	8.00	7.18	6.58
Ar	4.99	3.22	2.78	2.39	2.24
Kr	4.03	2.34	1.98	1.12	1.44
Xe	.....	.....	1.50	1.12	0.99
H_2	13.3	13.6	13.5	13.4	13.4
N_2	4.21	3.04	2.70	2.39	2.25

As stated before, in the more polarizable inert gases the mobilities can be computed by Langevin's approximate formula, which incidentally is very close in the values it yields to the equations of Hassé. The comparison of theory and experiment is in this case exceedingly close as shown by Powell and Brata in the table below.

Gas	Li^+		Na^+		K^+		Rb^+		Cs^+	
	Experiment	Theory	Experiment	Theory	Experiment	Theory	Experiment	Theory	Experiment	Theory
Kr	4.03	4.03	2.34	2.42	1.98	1.98	1.61	1.58	1.44	1.47
Xe	....	3.22	....	1.86	1.50	1.50	1.12	1.19	0.99	1.01

Actually it is not certain that these values of Tyndall and Powell and Powell and Brata are correct. Loeb[77] observed values in N_2 and H_2 which were somewhat above the values observed by Tyndall and Powell, giving $k = 17.5$ for Na^+ in H_2 and $k = 3.75$ for Na^+ in N_2. While Powell and Brata's gases were probably purer than Loeb's, and his method was open to a source of uncertainty in the correction for gas density, it is seen that his values are also fairly close to the computed values on the theory. It seems, however, as if the values of Tyndall and Powell are more likely to be correct, in which case there is a discrepancy with theory yet to be accounted for.

On the whole, however, the agreement observed seems far better than might be expected with the present lack of knowledge.

The fact is that it is rather much to expect the D observed for gases in bulk in weak fields to be unchanged when the strongly divergent fields of the order of 10^8 volts/cm in the immediate neighborhood of an ion are encountered. The ordinary law of dielectric displacement obviously cannot hold where the distorting forces of the ionic field at points approach those sufficient to cause a change of charge between ion and molecule. That the equations using the value of D from low field measurements is as successful as it appears to be must be ascribed to the observation by Tyndall and Powell that, in general, most of the encounters of ions causing loss of momentum in the field are the force-field encounters which do not involve the close approach of the elastic impacts.

That the law is further not justified in close approach of ion and molecule follows from the observed difference in mobility of positive and negative ions. The $D - 1$ terms do not distinguish between positive and negative ions, and thus the forces cannot depend on the sign of the charge on the ion. Yet experiment shows that the mobilities for differently charged ions in different gases vary very decidedly.[71] This difference was ascribed to the formation of specific complex ions with molecules of the gases present and these are quite charge-sensitive. Such action *cannot* thus *be ascribed to the ordinary dielectric attraction, and the clustering observed is not a clustering due to the dielectric forces.* It is a complex ion formation of specific electrochemical character in which certain chemical groups are oriented by the charge in such a way that a type of chemical binding takes place. Such complex ion formation thus is quite able to explain the difference in mobility of the negative and positive ions and to indicate that a more accurate knowledge of the mobilities of the ions requires a more precise knowledge of the laws of force acting between ions and different types of molecules at close approach. With this indication of the limitation of the ion theory, one may leave the subject of the ionic mobilities.

107. The Coefficient of Recombination of Ions.—When the first edition of this text was written, the problem of the recombination of ions was in a most unsatisfactory state, due to lack of adequately controlled quantitative information, much of which has recently come to hand through the application of the improved technique now available as a result of the development of X-ray sources. In what follows, therefore, much of the earlier

work will be omitted and only the more recent results and conclusions given.

It was early observed that the ionization produced by X-rays in a gas gradually disappeared with time. This was at once ascribed to two effects: the one, diffusion of the ions to the conducting walls of the vessel, and the other to a recombination of the ions of opposite sign due to their mutually attractive forces. The phenomena of loss by diffusion are phenomena requiring a relatively large ratio of wall surface to gas volume for their study. In the case of recombination, the phenomenon is a volume effect and diffusion must be reduced to a minimum. Since the ions of opposite sign are in general created in a gas space in equal numbers, and since the loss of ions dn in a time dt depends on the encounter of the ions of opposite signs, one can, calling n_+ the number of positive ions in unit volume and n_- the number of negative ions in unit volume, write that $n_+ = n_- = n$ and that $dn = -\alpha n_+ n_- dt = -\alpha n^2 dt$. Here the negative sign indicates that n decreases as t increases, and α is a constant of proportionality called the coefficient of recombination, a characteristic of the ions and the recombination mechanism. This equation implies another factor in assigning values to n_+ and n_-, to wit, the concentrations of the ions. It implies that ions are distributed at random in the volumes and that the volumes are large enough so that in general the average concentrations are represented by n_+ and n_-. An arrangement of ions in space so that positive and negative ions are grouped in pairs[42] would not be in accord with the above law, for this would give fictitious values to n_+ and n_- which vary with time due to diffusion, irrespective of recombination. With this precaution in defining n_+ and n_-, one may integrate the expression and evaluate n as a function of t. Integration between the limits $n = n_0$ at $t = 0$, and $n = n$ at $t = t$ gives the equation

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t, \text{ and } \alpha = \frac{1}{t n_0}\left(\frac{n_0 - n}{n}\right).$$

If the quantity α should for any reason fail to be a constant in time, the equation would not properly serve to define α as it would give the average value of α from 0 to t. If α is not constant, the quantity α_t must be determined. Assume n_{τ_1} to be the concentration at $t = \tau_1$ and n_{τ_2} to be the concentration at

$t = \tau_2$, α_t will then correspond to an average time $t = \frac{\tau_1 + \tau_2}{2}$, the interval $\tau_1 - \tau_2$ being made as short as experimentally possible. α_t is then found experimentally from

$$\alpha_t = \frac{1}{(\tau_2 - \tau_1)} \left(\frac{n_{\tau_1} - n_{\tau_2}}{n_{\tau_1} n_{\tau_2}} \right).$$

It is only in recent years that a system of measurement has been devised which gives controlled intensities of ionization sufficient to give good values of α_t.

All earlier measurements had indicated that α was apparently constant with time. What changes in α with t had been observed were ascribed to a loss of ions by diffusion. The values of α obtained were, strangely, nearly the same for all gases despite the fact that the mobility of the ions in these gases differed widely. Two observers, Rümelin[50] and Plimpton,[37] did observe that α was high for values of t which were short. Rümelin ascribed this to the effect of electron recombination with ions in the shorter time intervals t when the electrons were free. This, as is today known, is incorrect, for electrons have a very small value of α and in fact attach to neutral molecules more readily than to positive ions. Plimpton's explanation was essentially correct and is in line with the more recent understanding of the problem. The whole question of the understanding of α and the interpretation of the results for a long time hinged on a fundamental point in the theory. Langevin[43] in 1903 developed the generally accepted theory of recombination. Strange to say, this theory had a very subtle error inherent in it. This error was unrecognized for nearly 25 years, although countless physicists including the author had studied, used and accepted the theory. It was not until a rival theory, based on apparently very different assumptions due to J. J. Thomson,[45] raised an issue, that Langevin's theory was questioned. The experimental justification of the Thomson theory in 1929[41] so forced further study that it brought out the cause of the error in the assumptions of Langevin.

Langevin assumed that the positive and negative ions *actively* attracted each other according to the inverse square law, $f = e^2/Dr^2$, for all distances of separation r in the gas. Under these conditions the ions should continuously and gradually drift together, the rate of drift increasing as r decreased. On

this basis Langevin deduced a theory assuming that one ion, *e.g.*, the positive ion, was *fixed* and the opposite ion moved towards it with the relative velocity of both ions under the electrical field of the fixed ion acting on the mobile ion. That is, he assumed the negative ion to move towards the fixed positive ion with the velocity $(k_+ + k_-)X$, where X was the field strength (e/r^2) at a distance r from the positive ion, and k_+ and k_- were the positive and negative ion mobilities. The resulting analysis gave for α the relation

$$\alpha = 4\pi(k_+ + k_-)e,$$

where e is the charge on the electron. This value was, however, too large, and Langevin* added a correction factor $0 < \epsilon < 1$ which took into account the failure of two ions, which had attracted each other, to recombine. He was then able to evaluate ϵ directly from his measurements on recombination, ϵ being a function of pressure and temperature. He could, however, find no satisfactory theoretical expression for ϵ.

Actually the reasoning above cannot be applied to ions in a gas under ordinary conditions. The error lay in assuming *one ion fixed* and the other in relative motion. Such an assumption will hold for a system of two isolated bodies immersed in a *homogeneous* viscous medium. Actually the air is not a medium of this type when regarded from the viewpoint of the ion, *for the ions are of the same dimensions as molecules and the ions are being buffeted here and there in a perfectly random fashion by molecular impacts.* Hence two ions in a gas are not an isolated system but are part of a medium which makes it impossible to consider one ion fixed and the other ion moving relative to it. In fact, at ordinary distances of separation from 10^{-2} to 10^{-5} cm apart at N.T.P., the ions are moved about at random by molecular impacts and will not have their motions seriously altered by the attractive forces between them, as the kinetic energy kT is $>> e^2/r$ at these distances. This situation was intuitively recognized by J. J. Thomson[45] when in 1924 he formulated his theory of recombination, although he did not point out that the conditions which he postulated made the Langevin theory untenable. Thomson assumed that in general at large distances between ions, due to the fact that the kinetic

* A full discussion of this appears in the first edition of "Kinetic Theory," p. 481 ff.

energy of molecular impacts on the ions was greater than the potential energy of the one ion in the field of its opposite, the random heat motions would determine the motion of the ions such that the ions would undergo a random diffusion, which in general must take them apart. Thomson, however, pointed out that at small distances r, such that $e^2/r \geq \frac{3}{2}kT$, the forces of attraction of the ions would become so great that the ions would be drawn together and recombine. He thus was able to calculate the rate (as a result of random heat motions) at which ions would diffuse into spheres about oppositely charged ions where active attraction occurred. This rate gave too large a value for α, and Thomson had then to compute a correction factor to take account of the chance that two ions, once they were close enough to actively attract each other, would succeed in effecting the transfer of the electron from one to the other. It is probable that this phase of the problem is one ultimately to be solved by wave mechanics, but for the present the classical theory of Thomson must suffice as no attempt has been made on the basis of wave mechanics.

That the Thomson equation is essentially correct in its viewpoint follows directly from the experimental results of Rümelin,[50] Plimpton,[37] and especially of Marshall.[41] It was proved by Plimpton and Marshall that the initially high fictitious values of α_t observed were due to an initial non-random distribution of the ions produced in ionization, and that, as time went on, α_t decreased as the distribution became more nearly random. This definitely indicates a diffusion of the ions initially generated in pairs to the random condition which can occur only if the ions separate. Marshall also showed that the fictitious value of α_t which varied with time in this region was dependent on concentration, an effect only to be expected on the viewpoint that the ions generated in pairs, in general, diffuse apart. The absence of the fictitious high values for α at short time intervals in H_2, where, owing to electron diffusion before attachment, the random condition is reached long before measurement, again confirmed this interpretation. The independence of α and the mobility of the ions also speak strongly against Langevin's theory, while it is in favor of Thomson's theory which stresses the mass of the ions in the recombination process rather than their mobility. Finally the aging effect in such a heterogeneous gas as air, where the average mobility changes only 10 per cent in an

interval from 0.01 to 1 sec. in time, while α changes in the same time by a factor of 3 as shown by Luhr, indicates that mass, *i.e.*, velocity of thermal agitation and not mobility k as predicted by the Langevin theory, determines α.

The discussion of the difficulty in the classical theory just indicated is open to mathematical demonstration in an approximate form through a study of the Brownian motion of two particles which attract each other according to the inverse square law of force as do two ions.[34] The problem is handled for the three-dimensional case and is quite similar to the treatment of the same problem in the one-dimensional case given in Sec. 88 with the exception of the added forces. The solution of the problem in this approximate form is due to Prof. Arnold Sommerfeld, who kindly assisted Loeb in the analysis of the problem when Marshall's results indicated a difficulty in Langevin's theory. Consider two particles 1 and 2 in a three-dimensional coordinate system subjected to unbalanced forces X_1 and X_2 because of unequal bombardment by the gas molecules.

Let u_1 = vector velocity of particle 1 = $\dot{w}_1$.
u_2 = vector velocity of particle 2 = $\dot{w}_2$.
w_1 = position vector of particle 1.
w_2 = position vector of particle 2.
B = the coefficient of viscous drag in the medium.
X_1 = unbalanced force on particle 1.
X_2 = unbalanced force on particle 2.
e = charge on ion.
r = scalar distance between ions.

$$(1) \qquad m\dot{u}_1 = -Bu_1 + X_1 + \frac{e^2}{r^2}\left(\frac{w_2 - w_1}{r}\right).$$

$$(2) \qquad m\dot{u}_2 = -Bu_2 + X_2 + \frac{e^2}{r^2}\left(\frac{w_1 - w_2}{r}\right).$$

Multiply (1) by w_1 and (2) by w_2. Then, since

$$w_1u_1 = \frac{1}{2}\frac{d}{dt}(w_1^2),$$

$$w_1\dot{u}_1 = \frac{d}{dt}(w_1u_1) - u_1^2,$$

it follows that

$$m\left[\frac{d}{dt}(w_1u_1 + w_2u_2) - u_1^2 + u_2^2)\right] = -\frac{B}{2}\frac{d}{dt}(w_1^2 + w_2^2)$$
$$+ X_1w_1 + X_2w_2 + \frac{e^2}{r^3}[(w_2 - w_1)w_1 + (w_1 - w_2)w_2].$$

Now

$$[(w_2 - w_1)w_1 + (w_1 - w_2)w_2] = [(w_2 - w_1)(w_1 - w_2)] = -r^2.$$

Taking the displacements for times which are sufficiently large, the positive and negative values of X_1w_1 and X_2w_2 must cancel out, and one can drop these two terms. Also $m(u_1^2 + u_2^2)$ is, on the average, $4(\frac{3}{2}kT)$ where k is the Boltzmann constant and T is the absolute temperature. Hence

$$(3) \quad m\frac{d}{dt}(w_1u_1 + w_2u_2) = -\frac{B}{2}\frac{d}{dt}(w_1^2 + w_2^2) + 6kT - \frac{e^2}{r}.$$

It is now necessary to find the time average of the integral of this equation over periods of time τ such that r does not vary by too large an amount; *i.e.*, it is required to know the velocity of diffusion for a given value of r. This is found as follows:

$$(4) \quad \frac{m}{\tau}\int d(w_1u_1 + w_2u_2) = -\frac{B}{2\tau}\int d(w_1^2 + w_2^2) + \frac{6kT}{\tau}\int_0^\tau dt - \frac{1}{\tau}\int_0^\tau \frac{e^2}{r}dt.$$

The integral $\int d(w_1u_1 + w_2u_2)$ vanishes for finite values of τ of the orders to be used in discussion, inasmuch as it is responsible for the transient term which in 10^{-5} sec. for Brownian particles ceases to exert any influence. Also let

$$\Delta_1 = w_1^2 - w_0^2 \text{ and } \Delta_2 = w_2^2 - w_0^2.$$

Then

$$\Delta_1 + \Delta_2 = w_1^2 + w_2^2 - 2w_0^2, \text{ and } d(\Delta_1 + \Delta_2) = d(w_1^2 + w_2^2).$$

It is also required to know r as a $f(t)$. Since, in general, this is a diffusion phenomenon, r may be expressed to a first approximation by the expression $r = r_0 + a\sqrt{t}$, where a is a constant. Performing the integration indicated and expressing the resultant logarithmic solution in terms of the first two members of its expansion in series, it is found, to a rough approximation, that

$$\int_0^\tau \frac{dt}{r_0 + a\sqrt{t}} = +\frac{\tau}{r_0}.$$

This leads to the result that

$$\frac{B}{2\tau}(\Delta_1 + \Delta_2) = 6kT - \frac{e^2}{r_0},$$

whence

$$\Delta_1 - \Delta_2 = \frac{2\tau}{B}\left(6kT - \frac{e^2}{r_0}\right)$$
$$= 2\frac{6kT\tau}{B}\left(1 - \frac{e^2}{6r_0kT}\right).$$

Now B for an ion can be found from the relation that the velocity $u = KX$, where K is the mobility, and the force on the ion $f = Xe = Bu$ when it moves in a field with a steady drift velocity. Whence $B = e/K$ and

$$\Delta_1 + \Delta_2 = \frac{2K}{e}(6kT\tau)\left(1 - \frac{e^2}{6r_0kT}\right).$$

As $N_Ak = R$, as $RT = PV$, and as N_Ae/V is Ne, the Faraday constant per cm^3, one can write that $KkT/e = N_AkKT/N_Ae = KP/Ne$. But it was found in Sec. 103 that $K/D = Ne/P$ so that $KP/Ne = D$, the coefficient of diffusion of the particle in the gas.

Hence it follows that

$$\Delta_1 + \Delta_2 = 2\left\{6D\tau\left(1 - \frac{e^2}{6r_0kT}\right)\right\}.$$

Thus, in general, after a time t when the ions are r_0 cm apart, the sum of the average squared displacements of the two ions in a time τ is given by the expression $\Delta_1 + \Delta_2$, and this is equal to the diffusion of uncharged particles $2(6D\tau)$ in a time τ except for a modifying or reducing factor given by the parentheses above. On the average $\Delta_1 + \Delta_2 = 2\Delta$, twice the average squared displacement of a single ion, and for the single ion it follows that there will be a random displacement given by

$$\Delta = 6D\tau\left(1 - \frac{e^2}{6r_0kT}\right).$$

Ignoring the parentheses, this is the well-known *diffusion* equation for a single particle in a time τ. The effect of the parentheses is to reduce this diffusion in the measure that $e^2/6r_0kT$ is important. While the equation is the result of an approximation and is not very accurate, so that the value of the constant is not accurate, the indication is quite clear. Since $\frac{3}{2}kT$ is the average kinetic energy of the molecules and ions, it is seen that the modifying term is merely the ratio of the potential energy of the two ions at a distance r_0 to 4 times the kinetic energy of

motion. If the two energies are comparable, the ratio approaches significant values and the diffusion is markedly retarded. When the ratio reaches unity, the equation becomes meaningless as the neglect of higher terms in the approximation cannot be ignored. It means physically that at this point the attractive forces overcome the random heat motions, and hence the ions come together.

This same problem was attacked several years later independently by W. R. Harper,[83] who proceeded to prove the diffusion to occur on the basis of a different type of reasoning. Both methods used are equally approximate and serve to prove that the conditions assumed by Thomson are correct. While on the Sommerfeld approximation the ions drift apart unless they approach to within $r_0 = d$ cm of each other, given by

$$d = \frac{e^2}{6kT} = \frac{e^2}{4KE},$$

Harper arrives at the criterion, good only when d is much larger than the mean free path, that $d = e^2/kT = e^2/\frac{2}{3}KE$. At 0°C. the values of d calculated from the criteria of Sommerfeld and Harper are, respectively, about 1×10^{-6} cm. and 6.1×10^{-6} cm. In any case it is seen that when the ions approach to within a critical distance d of each other in which at the temperature existing the kinetic energy of agitation is of the same order of magnitude as the potential energy due to the charges on the ions, there will be, on the average, active diffusion of the two ions together, while beyond this, on the average, a retarded diffusion apart will occur.*

Thomson[45] considered the problem of recombination as follows. If two bodies attract each other according to an inverse square law of force and are left to themselves, three types of orbits about their common center of gravity are possible. If the kinetic energy of approach is greater than the potential energy, the orbit will be an hyperbola and the two bodies will separate. If the energies are equal, the orbits will be parabolic and the

* It is important to note that while this consideration applies specifically to the case of two ions analogous reasoning can be applied to two molecules attracting each other or in fact to a molecule in any force field. It explains why two attracting molecules do not coalesce unless the potential energy at contact is greater than the kinetic energy of the gas, and why in the earth's gravitational field gas molecules form an atmosphere while large particles fall to earth. In these cases random motion will rule, and the particles will act like a gas until roughly the potential energies equal or exceed the kinetic energies.

bodies will just escape to infinity. If the potential energy is greater than the kinetic, the bodies will describe ellipses, *i.e.*, closed orbits. Now a closed orbit of this type, while offering no assurance that the electron of the negative ion will jump to the positive ion, would make such a recombination process more probable as it prolongs the period during which recombination may take place. Thus J. J. Thomson sets as his criterion for the recombination of two ions that they shall describe closed orbits about their common center of gravity. If left to themselves in space, the initial velocities of the ions would determine the orbits described. However, in the gas, one has the ions continually disturbed by thermal impacts of average value $\frac{1}{2}mC^2 = \frac{3}{2}kT$. Thus until the ions are within a distance d of each other, where d is evaluated by $e^2/d = \frac{3}{2}kT$, the kinetic energy will be greater than the potential energy. It is seen that the sphere of radius d here defined is about the distance between ions at which retarded random heat motion gives place to active attraction between ions. At 0°C. it is about 4.18×10^{-6} cm, or somewhat less than a mean free path in radius. Starting at the surface of a sphere of radius d about an ion 1, an ion 2 of opposite sign will on the average have a kinetic energy such that if neither ion 1 nor 2 has any energy losses while they are separated by less than d, they will just escape to infinity along parabolic orbits. In general, however, the ions approaching to within d will have some residues of their previous energies produced by the field e^2/r over the last free path before d is reached added to the energy $\frac{3}{2}kT$ of agitation. Hence of the ions of types 1 and 2, approaching within d cm of each other, only those will describe closed orbits about their common center of gravity (*i.e.*, recombine) which can lose energy gained from the field through impacts with neutral molecules while inside the sphere of radius d. This is a very crude criterion, but it defines the problem. It might be added that a single impact of one of the ions might not suffice, and a more adequate criterion would be that both the ions 1 and 2 should suffer an impact, or that one suffer two impacts. In any case it is clear that the problem of calculating the coefficient of recombination consists in calculating how many of the ions 1 and 2 drift into spheres of radius d from each other per second and then calculating the fraction of those that have either one ion or both ions colliding with neutral molecules within the sphere. Con-

sider an ion of type 1, *e.g.*, a positive ion existing at a density of n_1 ions per cm^3 in the gas and having a velocity of thermal agitation C_1. The negative ions will be characterized by n_2 and C_2. The relative velocity of the two ions will be given on the average by $\sqrt{C_1^2 + C_2^2}$. In 1 sec. an ion of class 1 will sweep out a volume $\pi d^2\sqrt{C_1^2 + C_2^2}$ cm in which any ions of class 2 encountered are liable to recombination. Hence the n_1 positive ions per cm^3 will in dt encounter $\pi d^2 n_1 n_2 dt\sqrt{C_1^2 + C_2^2}$ negative ions of class 2 in such a way as to give possible recombinations. It next becomes essential to calculate the chance of recombination w due to the loss of energy of ion 1 or ion 2

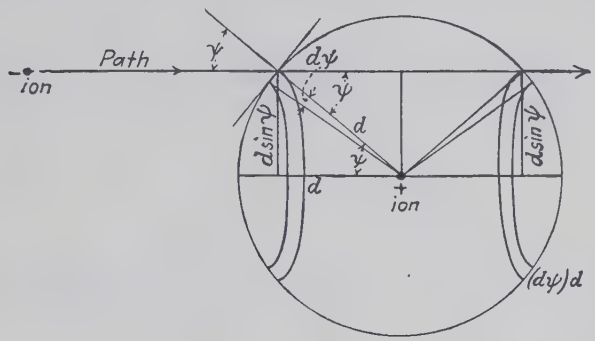

Fig. 74.

within d. Consider an ion of the type 1 of mean free path L_1. In sweeping out a volume of the last type, it will encounter ions of the opposite type 2 of free path L_2 traveling with the relative velocity along a path such as indicated in Fig. 74. This ion 2 has a path which strikes the sphere of radius d about ion 1 such that it makes an angle ψ with the normal to the surface of the sphere about ion 1. Such an ion as 2, provided the forces do not curve the path, will travel a length x inside the sphere given by $x = 2d \cos \psi$ as is easily seen. Actually in the intense fields within d the paths will be curved, and one can expect errors due to the assumption. The introduction of a curved path would, however, give refinements that would not be warranted on the basis of a theory as rough as this must be. The chance of an impact in a path of this length is given by the distribution of free paths as $e^{-\frac{x}{L_2}}$. Now an impact at an angle ψ on the sphere about ion 1 is not equally probable over the surface. In fact, it depends on the relative area of

a zone between ψ and $\psi + d\psi$ and the base of the hemisphere. This zone is drawn on the surface of the sphere of radius d about the line parallel to the relative motion of the ion through the center of ion 1. The probability however does not depend on the area of the zone but on this area projected on the normal to the direction of motion. The relative area of the zone, therefore, is given by

$$\frac{2\pi d^2 \sin\psi d\psi}{\pi d^2} = 2 \sin\psi d\psi,$$

and the projection of this on the normal to the motion of ion 2 is $2 \sin\psi \cos\psi d\psi$. Hence the chance of ion 2 escaping a molecular collision in sphere d about ion 1 at an angle ψ is $2e^{-\frac{x}{L_2}} \sin\psi \cos\psi d\psi$. The chance of escaping collision for all angles ψ is the integral between 0 and $\pi/2$ of the chance of escape at ψ. This is given by

$$2\int_0^{\frac{\pi}{2}} e^{-\frac{2d}{L_2}\cos\psi} \sin\psi \cos\psi d\psi,$$

which can bè easily integrated by remembering that $d(\cos\psi) = -\sin\psi d\psi$ and calling $\cos\psi = u$. Thus the chance of *escaping collision* is

$$\frac{2L_2}{2d}\left[\frac{L_2}{2d}(1 - e^{-\frac{2d}{L_2}}) - e^{\frac{2d}{L_2}}\right],$$

and hence the chance of *colliding* and thus of recombining is

$$w_2 = 1 - \frac{2{L_2}^2}{4d^2}\left\{1 - e^{-\frac{2d}{L_2}}\left(\frac{2d}{L_2} + 1\right)\right\}.$$

Analogously the chance of an ion of type 1 encountering a collision with a neutral molecule within a distance d of an ion of type 2 will be given by

$$w_1 = 1 - \frac{2{L_1}^2}{4d^2}\left\{1 - e^{-\frac{2d}{L_1}}\left(\frac{2d}{L_1} + 1\right)\right\}.$$

The chance that both simultaneously suffer collisions within d is merely $w_1 w_2$. Hence the number of recombinations dn in a time dt will be given at once by the product of $\pi d^2 n_1 n_2 dt\sqrt{{C_1}^2 + {C_2}^2}$ and the quantity $(w_1 + w_2 - w_1 w_2)$. This follows since the chance of loss of energy of ion 1, w_1, counts all losses for ion 1

and w_2 counts all losses for ion 2, whence the sum of $w_1 + w_2$ counts the simultaneous losses w_1w_2 twice, so that w_1w_2 must be deducted. Hence

$$dn = -\pi d^2 n_1 n_2 dt \sqrt{C_1^2 + C_2^2}(w_1 + w_2 - w_1w_2)$$

but

$$dn = -\alpha n_1 n_2 dt \text{ by definition of } \alpha.$$

Hence,

$$\alpha = \pi d^2 \sqrt{C_1^2 + C_2^2}(w_1 + w_2 - w_1w_2).$$

It was stated that probably one impact of either ion 1 or ion 2 with a molecule was not sufficient to cause recombination. The computation of w_1^2 and w_2^2 for two impacts each has been carried out with a slight error by Richardson.[44] However, since the curvature of the paths is neglected, such a calculation seems futile. An approximation to that sort of criterion which is at hand is the chance w_1w_2 that both ions suffer one impact with molecules in the sphere d. In this case α_L would be given by

$$\alpha_L = \pi d^2 \sqrt{C_1^2 + C_2^2}(w_1w_2)$$

and, if one assume $L_1 = L_2 = L$, which with the approximate nature of the theory suffices, one has

$$\alpha_L = \pi d^2 \sqrt{C_1^2 + C_2^2}\left[1 - \frac{L^2}{2d^2}\left\{1 - e^{-\frac{2d}{L}}\left(\frac{2d}{L} + 1\right)\right\}\right]^2.$$

The quantities $w_1 + w_2 - w_1w_2$, neglecting the w_1w_2 in Thomson's equation for α and the $w_1w_2 = w^2$ in α_L, can be represented[34] by curves as a function of $2d/L = x$, and as

$$d = \frac{e^2}{\frac{3}{2}kT} = 4.05 \times 10^{-6}\frac{273}{T},$$

and as

$$L = 1 \times 10^{-5}\,\frac{760}{p}\,\frac{L}{L_A},$$

where L/L_A is the value of L relative to L_A, that for air at N.T.P.

$$x = 0.81\frac{T}{273}\,\frac{p}{760}\,\frac{L_A}{L}$$

for a gas at constant density with p in mm of Hg, and T in degrees absolute. The values of $w_1 + w_2 = f(x)$ and $w^2 = f(x)^2$ are shown in curves 1 and 2 of Fig. 75 for a range of x covering experimental measurements. Again $\sqrt{C_1^2 + C_2^2}$ is the relative

velocity of the two ions, and, as in absence of any precise knowledge it is simpler to write $C_1 = C_2$,

$$C_1 + C_2 = \sqrt{2}\sqrt{\frac{2}{M}}1.84 \times 10^5\sqrt{\frac{T}{273}},$$

where M is the molecular weight and 1.84×10^5 is the velocity of agitation for the H_2 molecule at 273° abs. Whence α from the two equations proposed becomes available for comparison with experiment as

$$\alpha = 3.8 \times 10^{-5}\left(\frac{273}{T}\right)^{3/2}\left(\frac{1}{M}\right)^{1/2} f\left\{0.81\left(\frac{273}{T}\right)\left(\frac{p}{760}\right)\left(\frac{L_A}{L}\right)\right\},$$

$$\alpha_L = 1.9 \times 10^{-5}\left(\frac{273}{T}\right)^{3/2}\left(\frac{1}{M}\right)^{1/2} f\left\{0.81\left(\frac{273}{T}\right)\left(\frac{p}{760}\right)\left(\frac{L_A}{L}\right)\right\}^2.$$

If one choose $L_A = L$, $M = 28.8$, and $T = 273$, the values of α obtained are

$$\alpha = 2.82 \times 10^{-6},$$
$$\alpha_L = 5.64 \times 10^{-7}.$$

Had one, as is more nearly correct, chosen $L = L_A/5$ (for the mean free path of ions is about one-fifth the kinetic-theory value

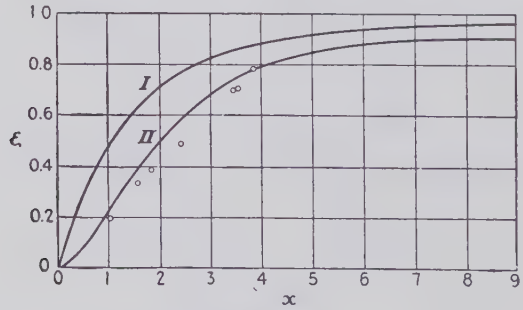

FIG. 75.

of that for molecules in air) and had one placed $M = 3(28.8)$ which is possibly more nearly the real mass of the ion, the values would become

$$\alpha = 8.41 \times 10^{-6},$$
$$\alpha_L = 1.62 \times 10^{-6}.$$

It is seen that the values of α_L lie more nearly in the region observed by Marshall than do the values of α.

As regards the variation of α with pressure, the results of Thirkill,[46]* the circled points in Fig. 75, agree fairly closely with α_L but are incompatible with those for α. In the case of the temperature variation Erikson's[48] results at constant density are compared with the theoretically predicted values of α after adjusting one value at 285°C. to correspond to Erikson's observed value. The agreement is indicated by the table.

Temperature in degrees C.	Observed	Calculated
94	3.18	5.1
205	2.39	2.16
285	1.47	1.47
337	0.94	0.90
373	0.74	0.75
428	0.59	0.53

The agreement is fair except at the lowest temperature. This may be due to a failure of the theory as regards the power of T to be used, the $\frac{3}{2}$ power being too high, or it may be due to an actual *increase in the size of the ion*, at such low temperatures, which makes $\sqrt{C_1^2 + C_2^2}$ really smaller than it appears and hence gives a low observed value of α. There is some possible evidence for this from the values of mobilities at liquid-air temperatures.

As is seen from the foregoing comparison, the Thomson theory agrees in the general trend of predicted behavior and in actual order of magnitude with the doubtful results of experiment. The situation concerning an adequate test of the theory by experiment is even more serious than that in the case of the ionic mobilities. At least in pure gases, in short time intervals for known positive ions, real data on mobilities can be obtained. In the case of recombination, nothing but "shot-gun" methods are as yet available.[47,34] α cannot be measured for times much less than 10^{-3} sec. by any *direct* method where the variables can be controlled. Even in the purest gases the ion forms attachment products in less than 10^{-3} sec. and is thus of uncertain mass. Also negative and positive ions both must be

* Thirkill used the method of Langevin, with ionization produced by X-rays, thus obtaining results which should be fairly reliable. Observations of other workers do not cover as wide a scope as those discussed here and consequently are not given consideration.

generated, which means positive and negative ion formation in pairs, and this initially does not give random distribution. Thus the values of α observed in the early periods of recombination are fictitious. In gases like air the progressive aging and formation of heavier ions together with a loss of the faster ions by recombination make the values of α still more variable with time and thus unreliable. Hence, to date, no measurements of α have been made in really pure gases which are known to be representative of any definite type of ion and which are known to yield a stable value of α. In the few early studies of the variation of α with pressure[46] and temperature,[48] with the existing ignorance of the variation of α with time, no measurements could have been made that insured that values of α came from the same point in the α time curve and were thus comparable, and it was not even certain that the values of α represented the same sort of ion at the various temperatures and pressures. Finally in the purest gases worked with, such as H_2 and N_2, the carriers in part were electrons, for which α_e is orders of magnitude different from α for ions. It is probable that in some of these cases the α observed may have been influenced by the rate of electron attachment to neutral molecules of impurities to make the ions thus still further compromising α for comparison with theory.

It is essential that with the present knowledge and improved facilities available, careful determinations of α in pure gases be undertaken, precautions being taken to make sure that the values correspond to the same ion and to the same relative values of α on the time curves, and care having been taken to eliminate the effect of the free electrons in the recombination. Perhaps such measurements should be accompanied by mobility measurements on the same gas with the same age of ion in order to insure constancy of the ion for variations in pressure and temperature.

In passing it must be pointed out that in recombination, in contradistinction to mobility, the essential factor is the average relative thermal molecular velocity $\sqrt{C_1^2 + C_2^2}$. This varies inversely as the square root of the mass of the ions. Thus, until the ionic mass is known, little progress can be made in an accurate study of the theory. It must be noted that, on this theory, the mobilities and recombination coefficients should not be closely related. This observed lack of parallelism between mobilities

and α is contrary to Langevin's theory but is expected on Thomson's theory, for k depends very little on M, while C depends essentially on M. The best values of α obtained so far are those of Luhr,[84] and these are open to some of the doubts expressed above, although the time factor has been corrected. They are as follows at 20°C. and 760 mm pressure.

O_2 $(1.32 \pm 0.1) \times 10^{-6}$
N_2 $(1.06 \pm 0.1) \times 10^{-6}$
Ar $(1.06 \pm 0.1) \times 10^{-6}$
H_2 $(0.28 \pm 0.05) \times 10^{-6}$
Air $(1.23 \pm 0.1) \times 10^{-6}$ at 5×10^{-2} sec. age.

Here it is seen that H_2 has a far lower value of α than O_2, N_2, or Ar, while in these gases the *mobilities* are far lower than in H_2. In part the value in H_2 is due to the unknown nature of the carrier of the charge. While initially the ionized carrier was H_2^+, by the time these measurements were made, the carrier probably had the mass of a molecule much greater. It is likely that the positive ion in relatively pure H_2 has a molecular radius of the order of that of the $H^+CH_3NH_2$ molecule and a mass correspondingly great. Hence the recombination coefficient observed for H_2 might be expected to be of the same order as those in N_2 or Ar, where similar positive ions exist after 10^{-3} sec. This appears to have been the case in less pure samples of H_2 used by earlier observers.[49] Luhr's[84] value in H_2 is, however, much *lower* than in these gases. This is to be ascribed to the fact that in Luhr's experiments in H_2 the electrons were largely free. In N_2 and Ar they should also have been free. Bradbury,[66] however, later showed that in Luhr's experiments with N_2 and Ar only about one-third of the electrons were free, while in H_2 the fraction was considerably greater.

This leads one to inquire into the value of α_e for free electrons and ask how it is that free electrons with a very high velocity of diffusion apparently recombine slowly with positive ions, for C_e is very high compared to C_1. The answer is easy to find. Even the heavy ions find it hard to recombine, *i.e.*, to describe permanent orbits about their common center of gravity, owing to the excess of energy gained from the field and the thermal impacts. In Thomson's theory at least one or two impacts with neutral molecules are needed to take up the energy to make recombination possible. In the case of electrons, as will later be learned, the impacts are very much more elastic and the

electron finds it very hard to lose its excess energy through impact. In fact, the only way in which the electron can lose its energy in the process of recombination is to fall into a vacant electron orbit in the positive ion and emit radiation whose frequency is determined by the relation $h\nu = h\nu_0 + \frac{1}{2}mv^2$, where ν_0 is the frequency for a free fall from infinity to the orbit in question and $\frac{1}{2}mv^2$ is the excess energy of the electron.[47] Such a radiation emission is a process whose *a priori* probability is exceedingly small. Thus the electrons remain uncombined in a gas. No direct observation of α_e for electrons has been made under conditions similar to those for ions. At very low pressures Kenty[85] has estimated α for electrons in Ar to be of the order of 10^{-10}. On the other hand, for molecules like O_2 the chance of *attachment* of electrons on impact, while a function of the velocity, is of the order of 10^{-4} at velocities near that of thermal agitation (see Sec. 109). In N_2, if pure, the probability should be 0, but, if molecules like Cl_2, where the probability of attachment may be 10^{-1} or greater, are present even in 1 part in 10^6, most of the electrons would have attached in 0.01 sec. Thus in most gases, even when supposedly pure, free electrons attach to molecules to form negative ions more rapidly than they recombine with positive ions. Even were the probability of recombination of electrons and positive ions commensurate with attachment to neutral molecules, in view of the greater concentration of molecules attachment would occur much more frequently. Thus, for instance, ion densities are rarely greater than to 10^7 ions per cm^3, which means in air at atmospheric pressures in a gas they are present in a concentration of 10^{-12}, while impurities even in the purest gases are present in concentrations of 10^{-7}. Hence, for equal probabilities of attachment and recombination, attachment would occur more often than electron recombination. Then, if recombination of *ions* is more rapid than the electron attachment, the apparent value of α will depend on the rate of ion formation. It is suspected that this was the process that gave Luhr's values in H_2. Further experiments on α in pure gases are now in progress in the Physical Laboratory of the University of California with a hope of clarifying this problem.

108. The Mobilities of Electrons.—According to the elastic-collision theory of Langevin[20,26] for the mobility of a charged carrier, derived in Sec. 103, the mobility of such a carrier is given by

$$K_e = 0.815\frac{e}{m}\frac{\lambda_1}{C_1}\sqrt{\frac{M+m}{M}},$$

where m is the mass of the carrier, C_1 the square root of its mean squared velocity, M the mass of the gas molecule, λ_1 the free path of the carrier, and e its charge. This equation should be applicable to the case of the electron where m is the mass of the electron, C_1 the square root of its mean squared velocity of agitation, and λ_1 its free path. Theoretically λ_1 is $4\sqrt{2}$ times the mean free path for the uncharged gas molecules (see Sec. 24). Actually electron free paths vary with velocity in a very complex fashion and over a wide range (see Sec. 25). In rigorous calculations these values should be used. The mean free path of the electron, due to its much higher velocity, does, however, not appear to be reduced by the presence of its charge, in the same way in which this holds for the ions. At any rate, it may for the sake of simplicity be assumed that the value of λ_1 for an electron is $4\sqrt{2}$ that of the molecules. It might then be expected that the mobility of the electron could be computed by assuming C_1 a constant given by the velocity of thermal agitation of the gas. Now this is not the case. Franck and Hertz[52] were among the first to show that the electron in monatomic gases makes almost completely elastic impacts with the atoms. The many investigations on radiation and ionization potentials have shown that this is largely true for all gases, unless the electron has an energy $\frac{1}{2}mC^2$, which is great enough to excite one of the electrons of the atom or molecule to emit light, or to remove that electron, that is, there seems to be no or little loss of energy on impact between electrons or molecules unless the electron has an energy $\frac{1}{2}mC^2 = h\nu$, where ν is the frequency of the light emitted and h is the Planck constant. For most gases $h\nu$ leads to an energy equivalent to a fall of potential of several volts, that is, to an energy of 10^{-12} erg. The reason for this is quite clear. Unless on an impact the energy of the electron goes to deform the atom or molecule, that is, to displace one of its electrons, its energy loss must obey the laws of elastic impact. The quantum theory says that the deformation cannot take place unless the electron has the quantum of energy to move one of the molecular electrons to one of the outer orbits. This it cannot do except under the conditions above. Now in an elastic impact the electron trans-

fers an energy to the molecules which depends on the relative masses. It is given by the relation[3,86]

$$f = 2\left(\frac{m}{M}\right)\left(1 - \frac{M\omega^2}{mC_1^2}\right),^*$$

where $M\omega^2/2$ and $mC_1^2/2$ are the average kinetic energies of molecules and electrons, m is the mass of the electron, M that of the molecule, and f the fraction of the energy lost at an impact. For the case where $C_1 >> \omega$, $f = 2\frac{m}{M}$. For an N_2 molecule and an electron, $f = 0.0000384$, and for the helium atom, it is 0.00027. Thus the loss of the energy is very small. An analogous mechanical example would be the loss of energy of a perfectly elastic tennis ball thrown against the side of a small boat, where, owing to the great mass of the boat, the loss of energy of the tennis ball to setting the boat in motion would be very small indeed. The very small energy transfer to a molecule by an electron explains why the electron only loses larger amounts of energy to electrons.

The question of inelastic impacts of electrons with atomic or molecular structures is, however, much more complicated than appeared at the time of the writing of the first edition. Franck and Hertz[52] had observed only *elastic* impacts in the inert gases and Hg at energies below the radiating or ionization potentials derived from their spectra. This was also found to be strictly true for He by Compton and Benade.[53] In theory it should be true for any atomic structure, although for some of the alkali atoms the radiation potentials lie at very low energies, *viz.*, about 1 to 2 volts. For molecular structures the case is different. The energy levels in most molecules, both electronic and otherwise, are very complex and in many cases not well known. In addition, the molecules have rotational energy and energy of vibration of the atoms in the molecule. Now, owing to the small mass of the electron, one would not expect it to be able to lose energy to the massive atoms in the molecule or to the molecule itself to cause energy losses to vibrational or rotational changes of state, even though rotational frequencies are in the

* This equation due to Compton[3] has recently been more rigorously calculated by Cravath[86] for the general case with Maxwell's distribution of velocities. It gives the numerical factor 2.66 instead of 2.00 given above and takes the form $f = 2.66\,\frac{mM}{(m+M)^2}\left(1 - \frac{M\omega^2}{mC_1^2}\right)$.

hundredths of an equivalent volt and vibrations in the tenths of an equivalent volt of energy. Regarded from this point of view it is true that the electron by direct impact cannot produce such changes as it has not mass enough. In an indirect fashion, however, the electron can lose energy to vibrational states. The vibrational levels are different in molecules as the electron levels change. The same is true of the rotational levels as those depend on the moments of inertia of the molecule, and this varies with vibrational and electronic states. It has been shown that perturbations produced in the electronic molecular structure by rapidly moving electrons whose energy does not suffice to change electronic levels in the molecule can cause changes in vibrational levels in the molecules. Hence, by changing for a short time the electrical conditions in the molecule while effecting no permanent electronic change, there is the chance, depending on the phase of the vibration existing at the instant, of producing vibrational energy changes. Thus the impacting electron which is unable directly to transfer energy to the vibrating atoms and which has too small an amount of energy to give to molecular electronic levels can still lose energy to the vibration in molecules, and these losses can be in volts or fractions of volts of energy. The probability of such energy losses, however, is rather small compared to the probabilities of radiating or ionizing impacts when the electron has the threshold energy for such effects. The mechanism of such losses is clearly described by the Franck-Condon[87] mechanism of dissociation and intensity distribution in band spectra by electron impact. Thus, unlike the atoms, molecules have some very low electron-energy states, O_2 having a metastable level at 1.62 volts and apparently another level at about 1 volt. In addition, vibrational transitions of all degrees of energy loss are possible when the molecule is perturbed by a slow electron. It is not strange then that Franck and Hertz found electron impacts in H_2 somewhat inelastic and those in N_2 badly so, while results in O_2 could not be achieved. H_2 and N_2 are free-electron gases, while O_2 attaches electrons to itself, thus giving "inelastic" impacts of still another sort. In O_2, thus, electrons lose energies very readily and Bradbury[74] has observed the inelastic impacts at 1.62 volts. The loss of energy of electrons in H_2 and N_2 has been studied by Baerwald[88] and the fractional loss f is of the order of 1 or 2 per cent per impact. In N_2 and CO the problem was studied in detail by

Harries,[89] who observed a class of inelastic impacts in which electrons suffered serious energy losses in rather rare impacts, which are well below the lowest electronic radiation levels. This accounted for the average energy loss determined by others in more statistically conditioned experiments. Thus one will find that, in all molecular gases, f will be greater than the value to be expected from elastic impacts such as occur with inert gas atoms. It is for this reason that electrons gain their higher terminal energies so easily in the inert gases and that these show correspondingly lower breakdown potentials than do the molecular gases.

With the low rate of energy loss, one can turn to the behavior of an electron in a gas where an electrical field of low value exists. Here between impacts the electron gains an energy Xed from the field X, where e is the electron and d the component of the electron free path in the direction of the field. This energy plus the energy of thermal agitation it retains at its impact, except for the fraction f, which it loses. As f is small, the energy will be practically that gained in the field. As this goes on over several free paths, the energy of the electron mounts higher and higher. The energy gained, however, results in an increased velocity, which, owing to the electron's small mass, is not directed along the field but takes on all directions which the random motions of the electron, as a result of the collisions, demand. Thus what really happens is that the electron gains in energy and velocity, but the velocity is not in the direction of the field but a randomly directed velocity, or a heat motion. The temperature of the electron in virtue of the external field increases above that of the surrounding gas molecules. This process will go on until the fractional energy loss multiplied by the average energy of the electron equals the average rate of gain of energy by the electron from the field. The electron then reaches a steady state when it loses energy at impacts as fast as it gains it from the field. It has then gained its *terminal* velocity in the field, and it has a terminal energy well above that of the gas molecules about it. If the field is cut off, it loses this gradually, eventually attaining equipartition. If the field is high, the electron may gain radiation energy before it reaches the terminal state. It may then collide inelastically and again start from rest. In the mobility measurements the fields are such that this never occurs, so that it will be overlooked.

Accordingly, in the mobility measurements where the electron gains its terminal speed very soon, the factor mC_1^2 is not the energy of agitation of the molecules of the gas but a much larger quantity. To Townsend[15] belongs the credit of having seen this first. He represents the value of C_1 as $\sqrt{k}C = C_2$, where k is the ratio of the energy of the electron in the field to the energy of the agitation of the molecules. This k he succeeded in evaluating from measurements which he made of the diffusion of electrons at low pressures. Thus he found for electrons in air the values given in the table below:

p in mm	X in volts/cm	$\frac{X}{p}$	k
18.5	40	2.16	24.0
12.0	30	2.5	26.0
1.8	4	2.2	24.0
3.7	40	10.8	46.0
1.8	20	11.1	46.5
0.95	10	10.5	45.5

These show that k is considerable and that it depends on the ratio of field strength X to pressure p. In the latter case the value by which C would have to be multiplied to give the true value would be about 6.8. It is obvious that the terminal energy and hence the factor k must vary with the field strength, the free path, and the value of the quantity f. The first attempt at a theory of this was made by Loeb[2] in 1921. Later Compton[3] took up the computation from the standpoint of his measurements on f and arrived at an interesting theory, which, in the absence of more definite information about some of the quantities entering into the equation (notably λ_1), leads to satisfactory agreement with Townsend's[54] results for electron mobility. In what follows, Compton's* treatment of the problem will be given. Compton starts, as was done above, from the Langevin equation for electron mobility

$$K = 0.815\frac{e}{m}\frac{\lambda_1}{C_1}\sqrt{\frac{m+M}{M}} = 0.75\frac{e}{m}\frac{\lambda_1}{\bar{c}_1},$$

* In an article by Compton[26] and Langmuir, Compton gives a new and much more rigorous derivation. This derivation is far more extensive than the one given above and there is little space for it in this text. It is more accurate but in principle and results differs little from the above.

as m is small compared to M. In a field X the average distance which an electron advances in a second in the direction of the field is KX. But $\bar{c}_1/\lambda_1$ is the average number of impacts made in 1 sec. Thus S, the average advance of the electron in the field between successive collisions, is

$$S = \frac{KX}{\frac{\bar{c}_1}{\lambda_1}} = 0.75\frac{\lambda_1^2 eX}{m\bar{c}_1^2}.$$

Converting

$$\bar{c}_1 = \sqrt{0.849}C_1$$

and calling $eU = \frac{1}{2}mC_1^2$, then $S = 0.441\,\frac{\lambda_1^2 X}{U}$.

U is thus the energy of the electron in equivalent potential drop. As was stated before, the fraction of the energy lost at each impact of an electron with a molecule follows from simple dynamics.[3] It is given by

$$f = 2\left(\frac{m}{M} - \frac{\omega^2}{C_1^2}\right) = 2\frac{m}{M}\left(1 - \frac{\Omega}{U}\right),$$

where Ω is $\frac{1}{2}M\omega^2$ in equivalent volts. The terminal speed may at once be computed, for in going a distance dx in a field the electron gains an energy $eXdx$, and it loses an average of feU at each of the dx/S intervening collisions. The net gain in energy is

$$edU = eXdx - feU\frac{dx}{S}.$$

Putting in the values of f and S from above,

$$\frac{dU}{dx} = X - 4.536\ mU\frac{(U - \Omega)}{\lambda_1^2 MX}.$$

To get the terminal speed, it need only be remembered that when this is arrived at, $\frac{dU}{dx} = 0$. Thus,

$$U_t = \frac{1}{2}\Omega + \sqrt{\frac{\Omega^2}{4} + \frac{\lambda_1^2 MX^2}{4.536m}},\ *$$

* Compton's[26] more recent equation gives U_t as

$$U_t = \frac{\Omega}{2} + \left[\frac{\Omega^2}{4} + \frac{\lambda_1^2 X^2(M + m)^2}{5.32Mm}\right]^{\frac{1}{2}}$$

including Cravath's[86] correction.

in equivalent potential drop. If this be transformed to terms of $\frac{1}{2}mC_2^2 = Ue$, and the mean energy of the molecules is given as $e\Omega = \alpha T = \frac{1}{2}MC^2$, and, if $C_2 = 1.086\bar{c}_2$, then

$$(\bar{c}_2)_t = \frac{1}{1.086\sqrt{m}}\left[\alpha T + \left(\alpha^2T^2 + \frac{\lambda_1{}^2MX^2e^2}{1.134m}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}.$$

For many cases $e\Omega$ or αT is so small that it can be neglected, so that

$$(\bar{c}_2)_t = 0.891\left(\frac{\lambda_1 Xe}{m}\sqrt{\frac{M}{m}}\right)^{\frac{1}{2}}.$$

Accepting $\lambda_1 = 4\sqrt{2}\lambda$, U_t may be computed as a function of X/p, the field strength in volts per cm divided by the pressure in mm of Hg. The results of such a computation for several gases are given below:

Gas	$\sqrt{\frac{M}{m}}$	λ_1(in cm)	U_t (volts)
He	85.9	0.1313	$5.30\frac{X}{p}$
Ar	271.5	0.0461	$5.86\frac{X}{p}$
H_2	60.8	0.0842	$2.40\frac{X}{p}$
N_2	227.4	0.0435	$4.65\frac{X}{p}$
CO_2	285.0	0.0290	$3.88\frac{X}{p}$
Hg	608.0	0.0135	$3.85\frac{X}{p}$

This table holds for X/p of such a value that U_t is considerably greater than a value of $\Omega = 0.0372$ volt, the mean velocity of thermal agitation. It also holds only below values of X/p where U_t is less than a critical potential for radiation. When an electron has the terminal speed under the conditions specified above, the average number of impacts per cm advance in the gas is given as

$$\frac{1}{S} = \frac{1.065}{\lambda_1}\sqrt{\frac{M}{m}}.$$

It is of advantage to know how rapidly the electrons acquire their terminal speeds, that is to say, how far from the cathode

they get before they acquire them. This is obtained from the value of

$$\frac{dU}{dx} = X - 4.536mU\frac{(U - \Omega)}{\lambda_1{}^2MX}.$$

Designating the constant $4.536\frac{m}{\lambda_1{}^2M} = \frac{4.536p^2m}{\lambda^2{}_{10}M}$ as α^2, and integrating from $U = 0$ at $x = 0$ to $U = U$ at $x = x$, then U at x cm from the cathode is

$$U = \frac{1}{2}\Omega + X\sqrt{\frac{1}{\alpha^2} + \frac{\Omega^2}{4X}}\,\frac{e^{2\alpha^2\sqrt{\frac{1}{\alpha^2}+\frac{\Omega^2 x}{4X^2}}} - 1}{e^{2\alpha^2\sqrt{\frac{1}{\alpha^2}+\frac{\Omega^2 x}{4X^2}}} + 1}.$$

If $X = 0$, $U = \Omega$, and if the field is so large that Ω may be neglected,

$$U = \frac{X}{\alpha}\frac{e^{2\alpha x} - 1}{e^{2\alpha x} + 1}.$$

When x is large, U approaches $U_t = \frac{X}{\alpha}$.

The distance d that an electron has to go so that its energy reaches a fraction ϕ of its terminal energy can be obtained by setting $U/U_t = \phi$ and solving for the particular value of $x = d$ required. It turns out that

$$d = \frac{1}{2\alpha}\log\frac{1 + \phi}{1 - \phi}.$$

The average number of collisions μ made in going x while getting its terminal speed is

$$\mu = \int_0^x \frac{1}{S}dx = \int_0^x \frac{U}{0.441\lambda_1{}^2X}dx,$$

for

$$\frac{1}{S} = \frac{U}{0.441\lambda_1{}^2X}.$$

From the equation for U, this is

$$\mu = \left(\frac{M}{4m}\right)[\log\,(2 + e^{-2\alpha x} + e^{-2\alpha x}) - \log 4].$$

Thus the average number of collisions μ made in acquiring ϕ is obtained by putting d for x in the above

$$\mu_\phi = \frac{M}{4m}\log\frac{1}{1 - \phi^2}.$$

These results are summed up in the following table. They are of use where the question of the terminal velocities of electrons enters in.

p, in mm	ϕ	He, d in cm	N_2,* d in cm	Hg, d in cm
760	0.1	0.00064	0.00057	0.00047
	0.2	0.00131	0.00115	0.00096
	0.5	0.00356	0.00313	0.00262
	0.9	0.00953	0.00840	0.00708
	0.99	0.01710	0.01507	0.01260
10	0.1	0.049	0.043	0.036
	0.9	0.724	0.638	0.533
1	0.1	0.49	0.43	0.360
	0.9	7.24	6.38	5.33

* These values theoretically apply to N_2. Actually, as shown on p. 603, these data have no significance owing to energy losses in N_2 to vibrational and other excitations.

From the value for U_t and thus $\bar{c}_{2t}$, the electron mobility can be at once obtained, for it is merely necessary to replace the C_1^2 of the Langevin equation for electron mobility by this factor to get K_e, the electron mobility. Thus K_e becomes

$$K_e = \frac{0.815e\lambda_1}{\sqrt{m}\left[\alpha T + \left(\alpha^2T^2 + \frac{\lambda_1^2MX^2e^2}{1.134m}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}}.*$$

When the terminal velocity is large compared with the molecular velocities, the equation reduces to the form

$$K_{e_1} = 0.842\sqrt{\frac{e\lambda_1}{X\sqrt{Mm}}} = 0.707\sqrt{\frac{e\lambda_1\sqrt{f}}{Xm}}.$$

The complete mobility equation in terms of α is then

$$K_e = \frac{0.815\ e\lambda_1}{\sqrt{m}\left[\alpha T + \left(\alpha^2T^2 + 1.76\lambda_1^2\frac{X^2e^2}{f}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}}.$$

It is seen here that the mobility is not a constant but is a function of X/p, for $X^2\lambda_1^2$ is $(1/p)^2X^2\lambda^2_{10}$, where λ_{10} is the mean free path at 1 mm. As X/p increases, it is obvious that K_e will decrease. Thus the velocity of the electron in a gas in an

* Compton's[26] new equation for electron mobility replaces 0.815 by 0.921 and 1.134 by 1.33.

electric field increases more slowly than proportionally to the field strength. It is obvious that the greater the inelasticity of impact (*i.e.*, the greater the fractional loss of energy at an impact f) the less the value of K_e will depart from a true mobility, and the more slowly K_e will vary with X/p.

The equation can be compared with experiment by remembering that $\lambda_1 = \lambda_{10}/p$. Doing this the mobility constant (the mobility reduced to 760 mm pressure and 0°C.) K_{e_0} is given by

$$K_{e_0} = \frac{2.54 \times 10^5 \lambda_{10}}{\left[1 + \left(1 + 1.355 \times 10^6 M \lambda^2_{10} \left(\frac{X}{p}\right)^2\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}}.$$ *

It remains, therefore, only to put in the values of M, λ_{10}, and (X/p) to get K_{e_0}.

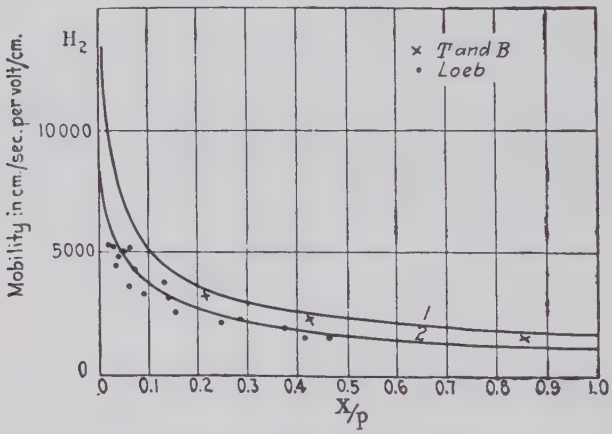

FIG. 76.

The results for H_2 are given in Fig. 76. The crosses represent Townsend and Bailey's[54] data, the points Loeb's[3] data, taken by a more direct but more fallible method. The mobility K_{e_0} is plotted as ordinates in cm/sec. against X/p in volts/cm per mm pressure. The smooth curves 1 and 2 represent the theory for $\lambda_{10} = 4\sqrt{2}\lambda_0$ for H_2 molecules, and $\lambda_{10} = 0.58\ (4\sqrt{2})\lambda_0$ for H_2 molecules. The former curve fits Townsend and Bailey's data better than does the latter.

* The most recent equation of Compton[67] differs only slightly replacing the 2.54×10^5 by 2.71×10^5 and the 1.355×10^6 by 1.106×10^6, and applying it to all temperatures T by multiplying the numerator by $\left(\frac{273}{T}\right)^{\frac{1}{2}}$.

The results in N_2 are given in Fig. 77. The results of the different workers are represented as before. In this case the one result of Townsend and Bailey in the region studied by Loeb agrees with his values fairly well. The smooth curve 1 is calculated from theory, assuming that the mean free path for N_2 has the value $4\sqrt{2}\lambda_0$ for molecules = 0.0405 cm at 1 mm pressure. This does not fit the data. By choosing $f = 0.05$, instead of 0.000038, the true value, curve 2, is obtained. This fits the data less well than curve 1. Finally, if f is taken as 0.000038 but λ_{10} is taken as $4(4\sqrt{2}\lambda_0)$, or 0.1620 cm at 1 mm pressure, curve 3 is obtained. This conclusion that the mean free path in nitrogen is longer than the kinetic-theory value was drawn by Loeb from his original measurements. The existence of abnormally long

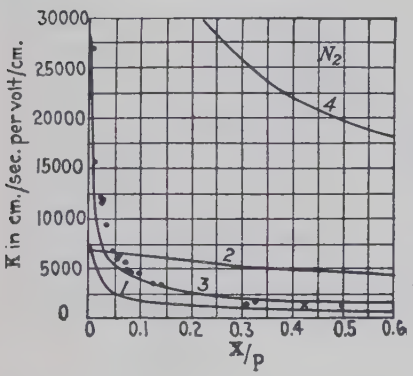

Fig. 77.

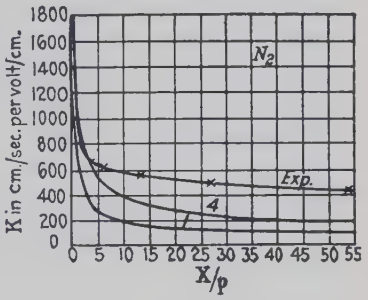

Fig. 78.

mean free paths of electrons in some gases has been shown by Ramsauer, Mayer, and Brode (see Sec. 25). They were not found in N_2 at the higher velocities worked at. It is possible that at the low terminal velocities at $X/p = 0.1$, where U_t is less than 0.4 volt, the N_2 which is similar to argon also shows abnormal mean free paths. The points at higher values of X/p and of U_t fall nearer the curve with the normal value of λ_{10}. Another striking confirmation of the theory was made by Wahlin[55] in N_2 at low values of X/p, that is, near 0.01, at the same time as Compton's paper was in press. The peculiar intercept of the theoretical curve with the axis of ordinates was experimentally observed in N_2 by Wahlin. The latter, however, treated his curve in a different manner theoretically. He finds that a λ_{10} which varies with velocity is needed. He also employs a higher f to attempt to get

agreement. This is justified by present knowledge, but the manner in which the energy loss should be applied may not be justified. Perhaps the best one can do is to apply the observed average energy loss inferred from experiment. Curve 4 in Fig. 77 is the case for N_2 when impacts are completely inelastic. It is seen that K is much higher than the observed values. In Fig. 78 the values of Townsend and Bailey at high values of X/p are given. Up to X/p equal to about 5, the curves fit fairly well. Beyond this the observed values are distinctly higher than the theory demands. Compton concludes that this represents an increase in f due to inelastic impacts, for here U_i is 23 volts in magnitude, which lies well above the ionization potential for N_2.

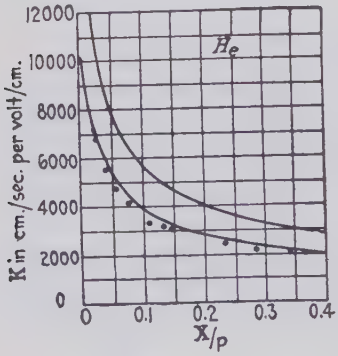

Fig. 79.

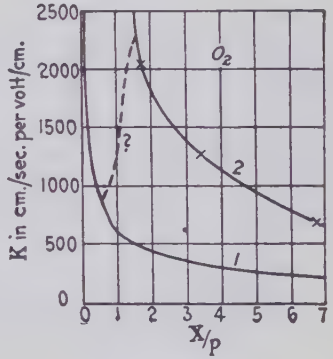

Fig. 80.

In Fig. 79 are given the results of Loeb in He. They are more in accord with the theoretical curve 2, for which λ_{10} is 0.5, the kinetic-theory value, than with 1, for which λ_{10} comes from the kinetic theory. The curve for O_2 (Fig. 80), represented by crosses, comes from the data of Townsend and Bailey. This is the worst failure of the theory, for using f and λ_{10} from the kinetic theory the computed curve is given by the full curve 1. Measurements in this gas, however, are highly questionable, as the electrons, on the average (in 40,000 impacts), attach to form ions. It is, however, quite possible that in this gas the electrons suffer less elastic impacts than in the other gases studied. A higher value of f would explain the result better than a higher λ_{10}. It may be noted that the measurements in O_2 correspond to about 8 volts' terminal velocity while energy losses are now known to occur as low as 1.62 volts, if not at still lower values.

The conclusion which can be drawn from the applications of the kinetic theory to the problem of electron mobilities is that the theory, in spite of the complexity of the problem, is more than qualitatively successful.

109. Attachment of Electrons to Neutral Molecules in Gases to Form Ions.—It was stated in Sec. 102 that the mobility of negative ions in gases was inversely proportional to the pressure down to very low pressures when ions that had been already formed were measured. Before the work of Wellisch[8,56] in 1915 this was not believed to be the case. It was observed by many workers that the mobilities of photoelectrically generated ions, measured soon after liberation from a metal plate in the measuring field, began to become abnormally great at 100 mm pressure in air. This was ascribed by numerous observers to a breaking up of the negative ion cluster by impacts with gas molecules. To Wellisch is due the credit for having investigated the mobilities of negative ions when formed behind a gauze, at low air pressures, after they had come through the meshes of the gauze. He found two classes of carriers, one which he showed were normal ions of a mobility constant close to the value accepted for normal negative ions, the other which he asserted were free electrons. The effect of the gauze and the weak auxiliary field back of it was to delay the photoelectrically liberated electrons, or electrons which were caused by radium radiations, until they formed ions. This Wellisch did not know. In fact, as he did not compare his results with the results of workers who had used no gauze, he devised another explanation. He assumed that an electron, when liberated, must have the energy ϵ_0 necessary to attach to a molecule to form an ion. If it has not this energy it will never attach and will remain permanently free. Thus one has either ions or permanently free electrons. In 1920, Loeb[9] undertook the problem and repeated Wellisch's experiments. He completely corroborated the observations of Wellisch. But he further observed that the relative number of ions and free electrons depended on the pressure and auxiliary field strength which allowed of only one interpretation. It showed that the free electrons were not permanently free. In fact, it showed that ion formation was contingent on the condition that the electrons spend a sufficient time in the auxiliary field before being studied. If the pressure and field strength were such that the time was short, only electrons were obtained; if the time was long, only ions were obtained. By

increasing the auxiliary field strength so that the electrons had a very high energy, no increase in the number of ions formed was observed by Wahlin,[51] who was then working with Loeb. Thus the Wellisch theory was found to be wrong.

The experimental work and viewpoint on this problem were very much aided by a theory of J. J. Thomson.[16] Thomson attempted to explain the abnormal increase of mobility of photo-electrically liberated ions at low pressures in air as follows. The ultra-violet light used liberates electrons. These do not attach to molecules to form negative ions at their first impact. If it be assumed that the electron requires, on the average, n impacts before it can attach to form an ion, where n may be a large number, then it is possible to explain the phenomenon. This amounts to assuming that the attachment of an electron is a chance phenomenon, depending on where it strikes the molecule or under what energy conditions the impact takes place. For each chemically different gas this would be different, depending on its chemical nature. For *simplicity*, Thomson assumed n to be a constant, independent of velocity, characteristic of each gas. That this is probably incorrect in some measure will be seen later. As a first approximation, it is, however, sufficient.

This constant n has other interests. Many discharge-tube phenomena had indicated that in certain gases the electrons apparently did not remain free, or were not present. In others they appeared to be so. It was Franck[57] in 1910 who first found that in carefully purified He the negative carriers had a mobility of several hundred cm/sec., while the positive carriers had the mobility of the normal ions to be expected in He. He interpreted these results as meaning that the negative carriers in He were free electrons. He found the same to be true in Ar and N_2 gases. In the latter gas he gave the value of 200 cm/sec. observed for the negative carriers as the electron mobility in N_2 at atmospheric pressure. It was the observation by Loeb on repeating Franck's work of mobilities of over 1,000 cm/sec. in N_2 which led to the electron-mobility investigations discussed in Sec. 108. Franck concluded from his investigations that the gases had electron affinities which varied with the chemical nature of the gas. This term was also associated with the electrical charge taken in polar compounds by the atoms. Thus, atoms like H, Na, Mg, or Al were called *electropositive*, while O and Cl were electronegative. That He and Ar, which are inert

gases, should leave the electrons free was not surprising. N in many cases, however, is chemically electronegative, while the N_2 molecule seemed to shun electrons as much as He. The more electronegative gases like O_2 and Cl_2 were, owing to their association with the electronegative atoms, considered to be admirable electron traps. This was borne out by their behavior in discharge tubes. It is, however, known today that the electropositive or electronegative character of an elementary atom is a property of the atom, due to the fact that the stable outer configuration of electrons in the atom seems to build around the number 8 in certain portions of the periodic table.[58] This striving towards completion of an octet, however, is definitely applicable to the atomic state. It depends on the nature of the electronic configuration of the molecule whether the addition of an electron to its configuration will increase its symmetry and therefore its stability or not. At the present time this is not predictable for molecules, and the association of electronegativity in the atomic sense with molecules is doubtful.

That electrons do make negative ions in some gases and not in others is, however, an observed fact which need have no relation to the atomic behavior above. The term electron affinity may then be applied to describe the behavior of a molecule towards the electron. It is then necessary to find more than a qualitative measure of this property. Two roads to this are open. The one would be to find out what the ionizing potential of the extra electron of the negative ion is. This, of course, could be determined by the frequency of the shortest wave length of the light emitted when an electron is attached to a molecule to form an ion. This multiplied by the Planck constant would give the energy necessary to remove the electron. Up to the present, investigations of this nature have yielded no result and one cannot measure electron affinity in this manner. The second procedure would be to get a quantitative measurement of the average number of the impacts required by an electron with a given type of molecule before it could attach. This quantity is precisely the quantity defined by J. J. Thomson as n, his constant of attachment. It is thus necessary to devise a means of determining this. If the number of impacts which an electron makes in going a given distance in a gas under an electrical field could be measured, and if the number of electrons, n_x out of N_0, that traverse a distance x in the gas in the field without attach-

ing could be measured, there would be a means of getting n, the constant of attachment. The number of electrons which go a distance x in a field without attaching must be derived from the assumptions as to n as related to the kinetic-theory constants before the value of n can be computed from any data. To deduce this expression, one may proceed as follows. Assume that it takes n impacts, on the average, for an electron to attach to a molecule, where n is a constant of the molecular type alone. If the average velocity of agitation of the electron is $\bar{c}_2$ and its mean free path λ_1, it makes $\bar{c}_2/\lambda_1$ impacts per second. If it is in a field of X volts per cm it moves K_eX cm/sec. in the field, where K_e is the electron mobility. It therefore takes $1/K_eX$ sec. to move a cm in the direction of the field, if it has its terminal speed (see Sec. 108). In this time it makes $\bar{c}_2/(\lambda_1 K_e X)$ impacts. Thus in going x cm in the direction of the field it has $x\bar{c}_2/(\lambda_1 K_e X)$ impacts. If attachment is purely a chance phenomenon, taking, on the average, n impacts for an attachment, the number dy out of y electrons attaching between x and $x + dx$ can be written as

$$dy = -\alpha y \frac{\bar{c}_2 dx}{\lambda_1 K_e X},$$

where the quantity $\bar{c}_2/\lambda_1 K_e X$ is the quantity by which the distance dx in the field must be multiplied in order to give the number of impacts in going dx cm. In this equation α is a constant to be evaluated from the equation obtained. Thus

$$\frac{dy}{y} = -\frac{\bar{c}_2 \alpha}{\lambda_1 K_e X} dx,$$

or

$$y = Ae^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x}.$$

If $x = 0$, $y = N_0$, the number of electrons starting, and thus

$$y = N_0 e^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x},$$

that is, y, the number of electrons going x cm in the gas without attaching, is found by multiplying the number N_0 starting at $y = 0$ by $e^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x}$. To get $\bar{x}$, the average distance the electrons go without attaching, one can write

$$\bar{x} = \frac{\int_0^{N_0} x dy}{\int_0^{N_0} dy},$$

and

$$dy = -N_0 \frac{\alpha \bar{c}_2}{\lambda_1 K_e X} e^{-\frac{\alpha \bar{c}_2}{\lambda_1 K_e X} x} dx.$$

Call

$$\frac{\bar{c}_2}{\lambda_1 K_e X} = \eta,$$

then

$$\bar{x} = \frac{\int_0^{\infty} - N_0 \alpha \eta x e^{-\alpha \eta x} dx}{\int_0^{\infty} - N_0 \alpha \eta e^{-\alpha \eta x} dx} = \frac{1}{\alpha \eta}.$$

But in going $\bar{x}$ cm the electron has $\bar{x}\,\eta$ impacts. Thus the average number of impacts which the electron makes before attaching is $\bar{x}\eta = \eta/\alpha\eta = 1/\alpha$. Therefore $1/\alpha$ is the average number of impacts which the electron makes before it attaches. This is n, the average number of impacts required to attach. Thus the number of electrons out of N_0 which go x cm without attaching in a gas is given by

$$y = N_0 e^{-\frac{\eta}{n} x} = N_0 e^{-\frac{\bar{c}_2}{n \lambda_1 K_e X} x}.$$

It is often more convenient to use this in another form, as λ_1 and $\bar{c}_2$ are not known. The equation for electron mobility says that

$$K_e = 0.815 \frac{e}{m} \frac{\lambda_1}{\bar{C}_2} = 0.75 \frac{e}{m} \frac{\lambda_1}{\bar{c}_2},$$

where λ_1 is the electronic path and $\bar{c}_2$ is the average velocity of agitation of the electron in the field. Thus

$$\frac{\lambda_1}{\bar{c}_2} = \frac{m K_e}{0.75 e},$$

and one has

$$y = N_0 e^{-\frac{0.75 e x}{m n (K_e)^2 X}}.$$

As $\frac{0.75e}{m}$ is 4.06×10^{17} in electrostatic units, and if K_e is to be

given in cm/sec. per volt/cm to correspond with X, this must be multiplied by 300; the equation reads

$$y = N_0 e^{-\frac{1.35 \times 10^{15} x}{n(K_e)^2 X}}.$$

The equation holds wherever K_e is known and n is constant. It must be pointed out that the value of K_e is usually measured or computed for electrons where $\bar{c}_2$ has reached a terminal value. In experimental attachment work where n is small this is not the case, and K_e must either be measured directly or else computed for velocities $\bar{c}_2$ that are not terminal velocities.

The first attempts made to measure n were due to Loeb,[17] and later to Loeb[59] and Wahlin.[51] The effect of the attachment and its consequent change of mobility of the carrier on the shape of the current-voltage curves obtained with a square-wave-form alternating current has been rigorously worked out by Mooney and Loeb. It is given, together with the attempt at experimental verification, in an article by Loeb.[59] The paper shows that it is possible to get a fairly accurate quantitative agreement using the uncorrected electron mobilities taken in air. With the introduction of the corrections to the electron mobilities, agreement is no longer possible. The reason for the lack of accurate agreement unquestionably lay in the variation of the attachment constant with electron velocity. Bailey, in Townsend's laboratory, measured the attachment constant n, or better its reciprocal, the probability of attachment h, by the analysis of the rate of loss of electrons and ions by lateral diffusion in a beam of what were initially electrons moving under a field in air at low pressures. He observed the values of h or n for air and found that these depended in a distinct fashion on the velocity, or, better, the energy of the electrons, h decreasing and n increasing as the value of the energy increased. Hence n or h is a function of X/p which must be included in the equations of Loeb in order to evaluate h. The complexity of the equations and the difficulty in obtaining accurate values of electron mobilities at higher pressures made an attempt to deduce the variation of h as a $f(X/p)$ from these data impossible.

Despite this fact these early studies yielded an approximate value of n for air in a given region of (X/p) which was of value, as it then was the only estimate of this quantity.[90] The terminal energy could not be calculated for these values of X/p in air, but even then the results served as a useful constant in discussions

of ionic behavior in the absence of more accurate data. The value of n deduced for air from these measurements was about 2×10^5. As electrons do not attach to N_2, these must all attach to O_2 molecules, and n for O_2 should be about 4×10^5.

At an earlier date before the values for electron mobilities were known at higher pressures, Loeb[17] and Wahlin[51] had measured n for a large number of gases. Using doubtful values of K_e, they arrived at the table of values for n given below. It is questionable whether the values are accurate in more than order of magnitude. They do differ, however, so widely in order of magnitude that even these crude early results give a good idea of n. In any case, they are the only estimates to date of this constant in different gases.[90]

ATTACHMENT CONSTANT n

Gas	n	Comment
N_2	∞	
H_2	∞	
CO	1.6×10^8	
NH_3	9.9×10^7	
C_2H_4	4.7×10^7	
C_2H_2	7.8×10^6	
C_2H_6	2.5×10^6	
CO_2	1.5×10^7	Freshly prepared
CO_2	3.5×10^6	4 hr. old
CO_2	2.1×10^5	22 hr. old
N_2O	6.1×10^5	
C_2H_5Cl	3.7×10^5	
Air	4.3×10^4*	
O_2	8.7×10^3	
Cl_2	Less than 2.1×10^3	

* The value of n for air was later redetermined using more accurate values for K_e. It is about 2×10^5. The value for O_2 was found to be one-fifth of this, in accord with the supposition that the electrons attached to the O_2 in air. The value 2×10^5 is in agreement in order of magnitude with recent more reliable values of Bailey.

While these results are not of more than qualitative value, they are significant, inasmuch as they give a definite though rough order of magnitude of the electron affinity of some gas molecules.

The difficulties in obtaining proper experimental values of n lie in the evaluation of K_e, which must be determined at the same time that n is measured. A further complication is introduced if n depends on $\bar{c}_2$. This is assumed to be the case by Bailey. Bailey[18] tried to overcome the difficulty in measuring K_e by obtaining measurements which determine the quantity $\bar{c}_2/n\lambda_1 K_e = \beta$ as a function of X/p. He did this by measuring the ratios of the currents passing through holes in a series of plates separated by known distances. The ratios of these currents can, by theory, be related to β, since the relative velocities of diffusion of electrons to the plates are greater than that for ions and can theoretically be computed. The measured ratios then give a factor β which measures the number of attachments per unit X/p per cm distance in the gas as a function of X/p. If β is known for a given X/p, then by using the relation $\frac{\bar{c}_2}{\lambda_1} = 0.75 \frac{e}{m} \frac{1}{K_e}$ one can get $0.75 \frac{e}{m} \frac{1}{(K_e)^2} \frac{1}{n} = \beta$, and hence $n = \frac{0.75\, e}{m} \frac{1}{\beta} \frac{1}{(K_e)^2}$. From the value of K_e or, better, $K_e X = W$, the velocity of the electron for the same value of X/p taken from the measurements of Townsend and Tizzard, n can be evaluated. In this fashion Bailey obtained $1/n$ for air for certain values of X/p as

$\frac{X}{p}$	0.5	1.0	2.0
$\frac{1}{n}$	3.3×10^{-6}	2×10^{-6}	0.7×10^{-6}
C_2	3.3×10^{7}	4.5×10^{7}	6×10^{7}

The corresponding values of C_2, ($0.92C_2 = \bar{c}_2$) for X/p are given below the values of $1/n$ as taken from Townsend and Tizzard's[54] results. They show that n has the values of 3×10^5, 5×10^5, and 1.4×10^6 in air at increasing values of C_2 of 3.3×10^7, 4.5×10^7, and 6×10^7 cm/sec. His results show that n increases as the velocity of thermal agitation increases. This means that n is not a constant of the chemical nature of the gas alone but depends on the average energy of agitation of the electron. That n should increase as the energy increases is not surprising, for it is to be expected that, as the electron travels faster, a capture is more difficult to effect. This is in line with Wahlin's results, who found that as the field increased the number of free electrons is not decreased as Wellisch's theory leads one to expect.

Since the first edition of this text was written, Cravath,[73] in Loeb's laboratory, applied a new method to the measurement of n or h devised by Loeb. In this a stream of electrons from a hot filament or other source is driven through a known distance x of air or gas at low pressure by an electrical field. At x cm from the source there is an equipotential surface having a grid of fine parallel horizontal wires separated from each other by 1 or 2 mm and insulated. Alternate wires are connected to the terminals of a high-frequency alternating supply of potential in the order of 10^6 cycles per second. This high-frequency field served to remove any of the very mobile electrons left in the beam after the distance x had been traversed, without removing the slow negative ions. The latter reached the other electrode creating the field, and the ratio of the current to the grid wires to the total current gave the fraction of the electrons which had not attached in the distance x. Using the data of Townsend and his pupils on electron mobilities in air at low pressures, Cravath was able to obtain h or n as a function of the terminal velocity or energy of the electron. His results lay close to those of Bailey in air, but in O_2 they extended to far higher values of X/p than did the previous measurements in air. Cravath found that h fell to a minimum at about 1 to 2 electron volts energy and started to rise again. He found that h appeared to vary with pressure when larger ranges of pressure were used. He also observed what seemed to be a detachment of electrons from negative ions in the intense fields about the grid wires when intense fields were used. The energy of detachment was about 0.9 volt as estimated from the fields.

The great defect in Cravath's method lay in having to use electron-mobility data from measurements not made on the same gases with which he was working. It also suffered from difficulties involved in the use of the absolute values of the currents to the grid and plate which required correction for loss of positive ions to the grid wires, the failure to capture all the electrons, etc.

Bradbury[74] in 1933 perfected an elaborate and beautiful method. He used two grids at distances x_1 and x_2 from the source. He used an outgassed all-glass system (this was the first time such purity had been achieved in the work) and photo-electrons instead of the contamination-productive hot filament. Finally he used a method of determining electron mobilities

to be described later, which gave results to far higher values of X/p than before and which were taken in the same chamber on the same gas and nearly concurrently with the attachment data. The use of the two grids eliminated the errors due to failure to capture electrons, and due to the capture of ions, by giving similar values due to these losses so that the relative current values for x_1 and x_2 gave the real ratio of ions and electrons. The results justified his pains. He found no pressure variation in O_2 but found that the curve for h as a function of energy fell rapidly to a minimum at about 1 volt electron energy and rose again at about 1.62 volts, reaching a maximum

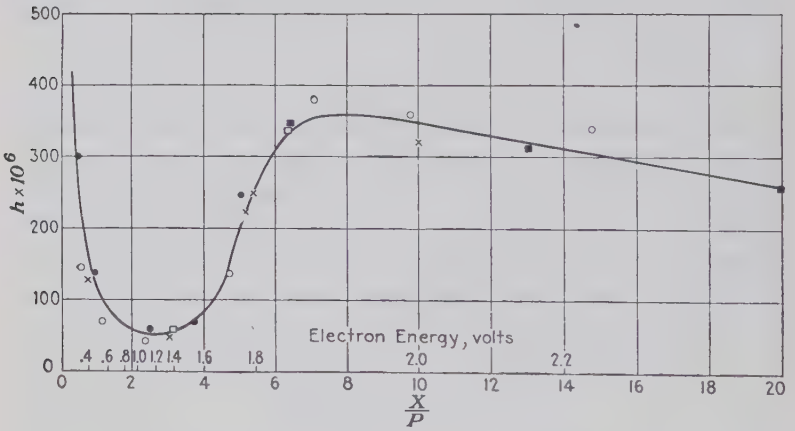

FIG. 81.

and then falling again. The rise at 1.62 volts was due to the fact that at 1.62 volts in O_2 the electrons lose energy to inelastic impacts and thus suddenly have an increase in h as the energy is decreased by inelastic impacts. Finally the average energy of the electrons increases again as they pick up energy in the field after the loss of the 1.62 volts and the curve ultimately falls. The observed curve is reproduced in Fig. 81. Studies in nitrogen-oxygen and argon-oxygen mixtures bear out his results and explain anomalies in the relative values of h in pure O_2 and mixtures observed by Cravath, which could not then be explained. Bradbury's values agree with the partial results of Bailey[18] and of Cravath[73] where they overlap. Bradbury also observed the detachment of electrons at high grid-wire fields observed by Cravath and at about the same energy. It is possible that this may lead to a method of obtaining the

electron affinities of neutral molecules on a true energy basis. Bradbury is extending the method to other gases. In general, then, it is seen that the concept of J. J. Thomson was a most fruitful one, as it has ultimately led to the successful explanation of many phenomena and may ultimately lead to a real evaluation of the energy of ion formation. The rough values of n estimated by Wahlin[90] are justified as order-of-magnitude estimates which must serve until further work, such as Bradbury's, gives more significant and accurate values.

110. The Photoelectric Current in the Presence of a Gas and the Theory of Ionization by Electrons.—It was stated in the introduction to this chapter that if electrons are liberated from one electrode in the uniform field of a plane-parallel condenser in the presence of a gas, the current rises at first in a nearly linear fashion as the field strength increases. Ultimately the current appears to approach a saturation value to be followed at high fields by a sudden increase due to the multiplication of carriers through the ionization of neutral molecules by impact in a field. It is of interest to study the rise of this current. As usual it will appear that the important parameter will be not the field strength X alone but rather the ratio of field strength to pressure X/p, where for convenience X is given in volts per cm and p is in mm pressure. The problem of the initial rise of the current was first solved many years ago by J. J. Thomson.[91] This approximate solution, although actually correct, appeared to give results which were not in accord with experiment. It transpired that this was no fault of the theory but lay in the interpretation of one of the terms in the equation, which should have been at once understood after the elasticity of electron impact was recognized. In this discussion the subject will be confined to the case of free-electron gases such as the inert gases, pure N_2 and H_2. For the case of the ionization by electron impact the gas discussed will be air because of the complete data at hand. In these discussions the intensity of the photoelectric emission of electrons will be considered so small that space-charge effects may be neglected as is the case where current densities of 10^{-13} amp. per cm^2 are encountered.

One may now consider the conditions when a field X exists across two plates of a plane-parallel condenser from which n_0 photoelectrons per cm^2 per sec. are being emitted by ultra-violet light, the space being filled with gas at a pressure p in which the

electrons remain free. In this gas the electrons have a mobility k_e which is their velocity per unit field but may be in turn a function of the field, as was seen in Sec. 108. The electrons emitted are drawn across the plates by the field X and yield a current per cm^2 which is given by $i = nk_eXe$, where n is the number of ions per cm^3, considered uniform between the plates.

Now in the gas space the electrons are moving among the molecules and, in the feeble concentrations present, act like a gas having the partial pressure which corresponds to the n ions per cm^3 present, the repulsive forces being negligible. Such a gas will show a tendency to diffuse back towards the cathode, and the number of electrons returning to the cathode which reach it and are thus removed from the current can be calculated by the kinetic theory from the relation of Sec. 40*a* which says that the number of molecules striking a cm^2 of surface per second is given by $\nu = n\bar{c}/4 = nC/\sqrt{6\pi}$, where C is the root-mean-square velocity. Thus the total emission current is partially lost by backward diffusion. Accordingly one can write that

$$n_0e = \frac{nCe}{\sqrt{6\pi}} + i,$$

where n_0 is the emission per cm^2 per second, $nC/\sqrt{6\pi}$ is the number of electrons lost by backward diffusion, and i is the current due to the movement of the electrons across the plates, these being the emitted electrons which have not been lost. Actually this assumes that the concentration of ions in the gas space is n all the way across the plates. This is not true, inasmuch as the emission and reflection of electrons as well as the diffusion in both directions together with the action of the field doubtless set up a very complicated distribution régime. Nevertheless, it happens that the simple assumptions lead to results in sufficient agreement with observation to warrant the rough approximation. Now it was shown that $i = nk_eXe$ so that, $ne = i/k_eX$, whence

$$n_0e = \frac{Ci}{(k_eX\sqrt{6\pi})} + i$$

so that

$$i = n_0ek_eX\frac{\sqrt{6\pi}}{(C + k_eX\sqrt{6\pi})}.$$

Since $k_e = (760/p)K_e$, one can write

$$i = \frac{n_0 e K_e \frac{X}{p} 760\sqrt{6\pi}}{C + K_e \frac{X}{p} 760\sqrt{6\pi}},$$

it being remembered that for electrons in a gas K_e is also a complex function of X/p. It is seen that, if $C << K_e \frac{X}{p} 760\sqrt{6\pi}$, $i = . n_0 e$, *i.e.*, the current approaches a saturation value, and if $C >> K_e \frac{X}{p} 760\sqrt{6\pi}$, *i.e.*, for low values of X/p, that i is nearly proportional to X/p, *i.e.*, that the current rises linearly. In any case i is a function of X/p that can be computed if $n_0 e$, C, and K_e are known. Now $n_0 e$ can be measured as it is the photoelectric saturation current which is easily obtained by pumping out the gas. It appears that with gases like H_2 or N_2 the effect of a change in the density of gas from that at atmospheric to 10^{-4} atm. does not materially alter the photoelectric emission if the light source is constant. When the metal is outgassed, on evacuation of the gas, however, the result would naturally be different. It was next observed that, while $n_0 e$ could be measured, when the gas was present the values of i were always very far below the value of $n_0 e$, no matter how high X/p (even into the region where ionization by collision begins). When the values of the electron mobilities K_e were available to test the theory in these gases, the observed results still did not appear to agree with the theory as it was applied. The difficulty was discovered by Loeb as Bradbury's[75] measurements under refined and stable conditions indicated the exact and serious nature of the departure. It had always been assumed that the electron velocity C would have the values appropriate to thermal equilibrium with the gas, since the electrons made many impacts with the gas molecules after liberation. It occurred to Loeb that it was probable that the loss of the electrons by backward diffusion must occur to the emitting plate. Now the electrons emitted by light from a quartz-mercury arc from a Zn electrode have an average energy in the neighborhood of 2 volts on emission. Before they can lose this energy, hundreds of impacts with N_2 or H_2 molecules are on the average required. These impacts will in general take the electrons far

from the cathode. Hence it is only the electrons with an average velocity given by $\frac{1}{2}mC^2 = \overline{h\nu} - h\nu_0$ for the photoelectric process which figure in the equation, where ν_0 is the photoelectric threshold and $\bar{\nu}$ is the average frequency of the incident light. This interpretation of the value of C at once gave the proper result. For, if C is of the order of about 2 volts, $C >> K_e\frac{X}{p}760\sqrt{6\pi}$ so that one is never near the saturation value as long as appreciable gas is present. When the gas density becomes so low that the plate distance is comparable with a few hundred mean free paths, the theory fails since the initial assumptions on which it was deduced do not apply. Another way of interpreting the significance of this assumption is to state that, in order that a large proportion of the electrons be saved from return to the plate, X/p must be such as to give an electron an energy of the order of a considerable portion of a volt in one free path. Before such fields are reached, however, ionization by collision sets in. Bradbury[75] inserted the proper value of C into his equations for i as a function of X/p and n_0e and by this means evaluated K_e, the electron mobility, as a function of X/p. In this fashion Bradbury checked the value of K_e of Loeb in N_2 and of Townsend and Bailey for H_2 in the region covered, within the accuracy of his assumed value of C. He was, however, able to go to far higher values of X/p than ever before, reaching $X/p = 20$ in H_2. Had the source of electrons been a hot filament and the current density been low enough to avoid space charges, the value of C would have been only some tenths of a volt instead of 2 volts.

As was seen above, the current will not reach a saturation value before ionization by collision sets in, and this will set a limit to the lower values of X/p at which one can accurately measure ionization by collision. This measurement of i and n_0e as a function of X/p thus not only establishes the theory but gives a new and fairly accurate method of obtaining K_e in gases. In his later measurements on the attachment coefficient h, Bradbury used this method for evaluating K_e making the photoelectric measurements needed to estimate C in the same chamber as was used for h.

In Fig. 82 are shown the saturation current n_0e in vacuum and the value of i as a function of the potential across the plates in H_2 gas at 3.0 cm obtained by Bradbury. In Fig. 83 the values of K_e obtained in N_2 are given as a function of X/p.

The circles and crosses represent data taken at two different pressures. Thus one has an explanation of the shape of the photoelectric electron current in a gas as a function of X/p.

In gases like air the case will be somewhat more complicated, due to electron attachment. This introduces two values of

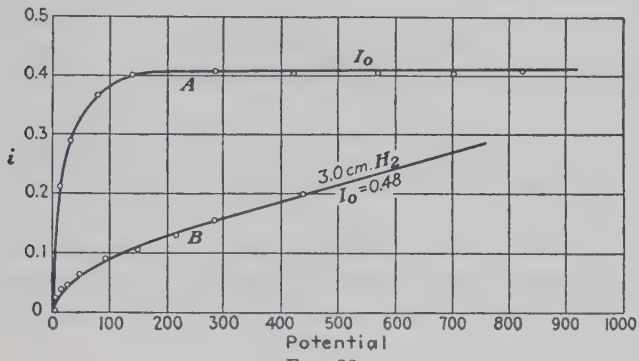

FIG. 82.

mobility into the equations, that of ions and that of electrons, the ions appearing to take the place of electrons as the charge moves through the field. The attachment will, however, little affect C, as the electron cannot as a rule attach very readily until its velocity is reduced. However, velocity reduction also

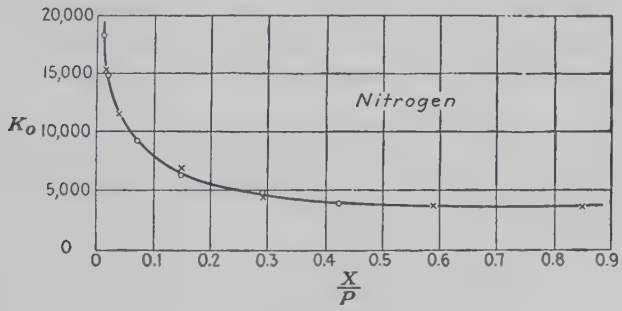

FIG. 83.

occurs more readily in gases where electrons attach. In general, Bradbury's results in air were not sufficiently different from those in the gases H_2 and N_2 to warrant any radical change in the equations except that one must remember that the value of C may remain the same, but K_e may reduce to ionic values at higher pressures.

One may now turn to the problem of ionization by collision. It was stated that when X/p became sufficiently great, the current began to increase exponentially. This increase was ascribed to the formation of new positive ions and electrons by the electrons initially generated. To Townsend,[19]* as was stated, belongs the credit for having investigated and explained the phenomenon and worked out the theory of the increase. His experiments showed that, for an initial saturation current i_0 at the surface of the plate $x = 0$, the current i at any distance x from the plate was given by $i = i_0 e^{\alpha x}$, where α is the number of ions generated per cm path by each of the electrons. This α was then shown by Townsend to be a function of the intensity of the field strength, the pressure p, and the energy required to produce an ion. This relation between α/p and X/p may be deduced as follows, according to Townsend. It can be assumed that the electron makes *inelastic* impacts with the molecules of the gas.†

Thus at each impact the electron starts its free path anew, gaining the energy from the field that it can gain on a free path. As the fields are high, it can be shown that the free paths of the electrons will be so curved in the field that their length will be mainly in the direction of the field. In order to ionize, it was assumed that the electron must strike the molecule with an energy E_0 gained from the field, that is, the energy gained by an electron that ionizes a molecule must be gained in the free fall of the electron through a distance λ_1 in the direction of the field given by $E_0 = Xe\lambda_1$ where λ_1 is the mean free path, X the

* Bergen Davis[92] in 1907 deduced an expression for α/p as a function of X/p along the same line as did Townsend but including the chance of energy transfer for an impact against a solid elastic sphere. As neither theory is correct on the basis of present-day knowledge and as Townsend's equation is simpler, it will be used for illustration.

† This assumption was originally made when it was believed that the negative ions, not the electrons, generated new ions by impact. It must now be abandoned, as will later be shown. In spite of the electronic nature of the carriers Townsend maintained that the velocity of the electron at impact with a molecule was reduced to the velocity of thermal agitation so that his theory remained unchanged for a long time. He later modified it to include more elastic impacts in He. Since, however, the theory is widely disseminated in present-day literature where it is available for use by those unaware of its weaknesses, these should be shown at this point. In addition, it serves as an excellent introduction to the problem as a whole. (See Townsend, "Electricity in Gases," p. 291, Oxford University Press, Oxford, 1915.)

field strength, and e the electron. Thus the number of ions per cm path generated by an electron must depend on the number of times, in going 1 cm in the gas in the direction of the field, that its free path equals or exceeds a distance x_e given by $x_e = E_0/Xe$. Now out of n_0 free paths the number of free paths exceeding a distance x is given by the kinetic theory as $n_0 e^{-\frac{x}{\lambda_1}}$, where λ_1 is the mean free path. Thus if in going 1 cm in the direction of the field the electron makes n_0 impacts with molecules then $\alpha = n_0 e^{-\frac{E_0}{Xe\lambda_1}}$. The number of impacts per cm path n_0 is simply $1/\lambda_1$ if, as assumed, the paths are in the direction of the field. Thus

$$\alpha = \frac{1}{\lambda_1} e^{-\frac{E_0}{Xe\lambda_1}}.$$

As $\lambda_1 = \lambda_0 \frac{760}{p}$, where p is in mm, one could write

$$\frac{\alpha}{p} = \frac{1}{760\lambda_0} e^{-\frac{E_0}{760e\frac{X}{p}\lambda_0}}.$$

Thus, α/p is a $f(X/p)$. For H_2 and one or two other gases Townsend measured α/p and, knowing λ, he was able to compute E_0 and test the theory.* The agreement observed was quite satisfactory and the value of E_0 deduced for several gases lay in the neighborhood of a free fall of an electron through a potential of 26 volts, that is, $E_0/e = V_0$ volts, where V_0 was about 26 or more volts. This measurement of the ionizing potential V_0 was the first estimate directly made.

The situation produced by the satisfactory agreement of the curves with the theory, however, leads to an interesting paradox, for, in the first place, the assumption on which this theory is based, to wit, that of inelastic electron impacts, is wrong. Also, the exact measurements of the ionization potentials at low pressures by such workers as Franck and Hertz and the countless other investigators in recent years[1c,60] show the values of V_0 computed by Townsend to be in the neighborhood of 50 or 100

* It must be noted that due to lack of facilities in this pioneer work, Townsend's data were taken at very low pressures, small plate distances, and high values of X/p. He did not go below $X/p = 40$ in air and most of his data lay above $X/p = 100$.

per cent too high. It might be added in passing that the essential difference in Franck and Hertz's[52] and Townsend's experiments lies in the fact that Townsend used far greater pressures. Thus his smooth curves are averaged over many free paths, while the low-pressure curves of Franck and Hertz show abrupt changes due to encounters over a single free path. In fact, as will be seen, the theory is far more complicated than it appeared to Townsend in the early days when his theory evolved. That the equation holds as well as it does merely shows that α/p is a function represented sensibly by $e^{-\frac{\gamma p}{X}}$, in Townsend's range of values of X/p, in which the value of γ was deduced from experiment by Townsend and interpreted in the light of his theory as giving values of V_0 of the order of magnitude obtained, that is, Townsend had an exponential form of equation that fairly well suited the facts, and he suited his adjustable constant V_0 to fit the equation by comparison with experiment.

In 1916, Compton[61] introduced into the problem the new fact, discovered first by Franck and Hertz[52] in 1913 and later carefully investigated for He by himself, that the electrons lost only a very small fraction of their energy on impact with neutral molecules. The considerations of the quantum theory show that there is no loss of energy in impact between electron and molecule unless the electron has the resonance or ionization energy except the fractional loss $f = 2m/M$ (where M is the mass of the molecule and m that of the electron), which is demanded by simple dynamics. If this is the case, then, as shown in Townsend's treatment of electron mobilities, the electron gains energy over several free paths, that is, its temperature goes up continually. Thus all electrons would gain the ionizing energy eventually. To carry the idea further quantitatively, Compton had to introduce another notion which was correct in theory. This is that the electron, while it could gain energy over several free paths, did not necessarily ionize on its first impact, but required perhaps many before it could ionize. As the probability of ionization by an electron with the energy E_0 or greater was not then known, Compton[61] arbitrarily assumed that the probability of ionization P_i had the form*

* Independently Bergen Davis[92] had deduced the same form of expression for P_i on the theory of solid elastic impacts. Compton's use of this factor was entirely independent of the latter theory and was based on similarity to the type of quantity observed and on considerations of convenience.

$$P_i = \frac{V - V_0}{V},$$

where V was the volt equivalent of the energy of the electron and V_0 the minimum ionizing potential of the gas. The theory which he deduced on the basis of these assumptions fitted the data for He with remarkable accuracy. In fact, it gave a better quantitative agreement than the theory of Townsend. Compton, however, did not have the true form for the function P_i as the later results of Hughes and Klein[62] and Compton and Van Voorhis[63] have shown.* The true curve of P_i against V does rise from 0 at V_0 to higher values at values of V considerably above V_0, but it later falls to lower values as V increases. Compton, however, neglected another effect. This is that, while the electron may gain the ionizing energy over very many free paths, it reaches an energy corresponding to the radiating energy long before it gets to V_0 for ionization. That is, if an electron gets an energy corresponding to 4.9 volts in mercury, it will suffer an inelastic impact sooner or later which does not cause ionization but merely causes the mercury atom to emit light of wave length 2537A. To ionize the mercury atom, the electron must have an equivalent energy of at least 10.6 volts. Thus if the electrons gain energy slowly, and if they make, on the average, 100 impacts in the region between the 4.9 and 10.6 volts required to ionize, an appreciable fraction of these electrons may lose their energy to inelastic radiating impacts. They will then have to start from rest again to ionize, that is, Compton failed to take account of the possibility of inelastic impacts between radiating and ionizing energies in his theory. The probability of a radiating impact with the requisite energy is not vanishingly small as shown by Sponer,[65] so that this must be taken into account. With He gas this chance is less than for any other gas, as its radiation potential is about 19.5 volts while its ionization potential is 24.5 volts. If the probability of radiating impacts

*Lawrence[64] has made carefully controlled measurements of the probabilities of ionization and of ionization potentials with electrons of an accurately known speed. He finds that P_i is highest just at the ionizing potential, falling off rapidly after that value. This, when carried over to other gases, will have a material influence on the theory above. For electrons with velocity distributions like those observed in this kind of ionization experiments the integrated type of curves such as obtained by Hughes and Klein and Compton and Van Voorhis will probably suffice.

in such a region were high, say, 0.5, Compton's theory would be untenable. The theory would then approach one of the original Townsend type. In this case, however, α would depend on the chance that an electron got the ionizing energy in a series of impacts so arranged that it had very few impacts in the radiating region. The first term of the series of exponential terms deduced on such a theory would be the one deduced originally by Townsend.

It is, obvious, however, from the small values of P_i and P_r, the ionization and radiation probabilities at the corresponding potentials (even though these may be the maximum values), that at fields where ionization by collision sets in the *factor which determines α is not so much the chance of getting the ionizing energy on one or more free paths but the chance of ionizing when it has that energy.* The solution of the problem of the value for α, therefore, lies completely in the future and involves the introduction into the equation of the little known probabilities P_i and P_r, as well as the rate of gain of energy from the field.

As was stated, Townsend's original investigations and those on which his conclusions were based were, owing to technical difficulties existing at that time, limited to low pressures, small plate distances, and high values of X/p. Thus, in the case of air, the gas of great importance from the industrial aspect of spark breakdown, data on α were obtained only down to $X/p = 40$, while but few points existed between this and $X/p = 100$. In He, Compton[53] had made measurements of a more modern nature. This gas, however, differs so radically from a gas like air that more complete modern data seemed imperative in order to aid in the explanation of short time lags and other problems of spark breakdown. To this end Sanders,[93] in Loeb's laboratory, built an apparatus capable of measuring α at plate distances from 1 to 10 cm instead of over a few mm, and at pressures around atmospheric pressure. This was possible because of the high degree of development of high-voltage technique in recent years (kenotron, rectifiers and high-resistance units for accurately measuring potentials). Under these circumstances with the aid of a grant from the National Research Council, Sanders was able to utilize the high sensitivity and resolving power of the larger air gaps to obtain values of α for X/p as low as 20 and to carry it in a continuous series of measurement up to $X/p = 160$ at which point his data coincided closely with

Townsend's more complete data. At the same time Paavola[94] and later Masch[95] made measurements at higher pressures but over small plate distances. Neither of the latter went below $X/p = 30$, but the results of Masch in the higher brackets closely agreed with the results of Sanders. At $X/p = 20$, calculations on Bradbury's[75] data showed that the rise of the current-distance curves due to unsaturation accounted for about half of Sanders' value of α. Thus Sanders showed that ionization by collision rises asymptotically from zero, and below $X/p = 20$ begins to be indistinguishable from unsaturation. The results of Sanders' study from $X/p = 20$ to $X/p = 36$ are shown in Fig. 84 in a plot of log (α/p) against X/p. The full curve is the least squares reduction of the observed values whose probable errors are shown as vertical lines.. It is thus seen that

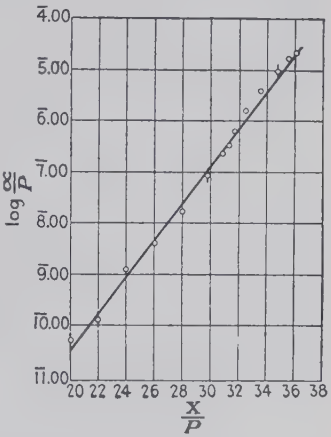

Fig. 84.

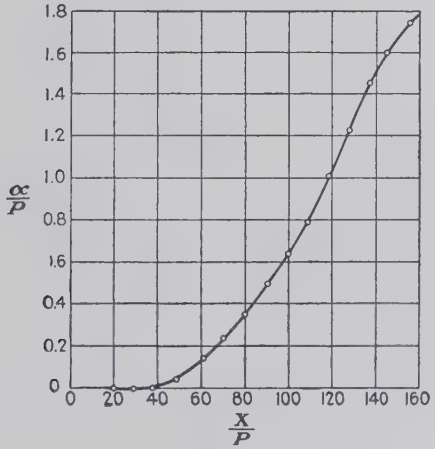

Fig. 85.

in this range $\alpha/p = Ae^{B\frac{X}{p}}$ with some degree of precision where A and B are constants taken from the curve, and of values $2.67 \pm 0.26 \times 10^{-8}$ and 0.350 ± 0.003 at 21°C. It was impossi-

ble to fit a curve of the Townsend form $\alpha/p = ae^{-\frac{bp}{X}}$ to these data. In Fig. 85 are shown the values of α/p plotted against X/p from $X/p = 20$ to $X/p = 160$. In this case it is seen that the logarithmic form for α/p as a $f(X/p)$ holding up to $X/p = 40$ begins to deviate from this law above this value, and α/p increases more slowly as X/p increases until it shows a tendency to reach a constant value. Above $X/p = 120$, Sanders found that the current-distance curves giving α/p showed a distinct deviation due to the assumed ionization by collision of positive ions. Townsend observed this phenomenon at higher values of X/p, which was to be expected due to the greater sensitivity of Sanders' experimental arrangement. Sanders tried to find an empirical expression for the curve from $X/p = 20$ to $X/p = 160$, but no simple relation was found. The conclusion to be drawn from this is that the curve is due to a series of different mechanisms following each other as X/p increases, of such complexity and interrelationship that a proper simple analysis is precluded. It is clear that the original Townsend theory does not hold for low X/p, as was to be expected from its derivation. At higher X/p the equations of Townsend may apply. It is probable that the first portion of the observed curve depends largely on the mechanism of the gain of energy by electrons which there occurs at such a slow rate that, once the electrons gain the ionizing energy, their impacts in this range are so near the threshold of ionization that many electrons gaining the energy ionize without losing their energy otherwise. Thus this part of the curve represents the increase in the number of electrons which acquire the ionizing energy in low fields as X/p increases. As the fields get higher, the electrons gain the ionizing energy more readily and lose less energy to radiation and inelastic impacts in consequence. They, however, find for the same reason greater difficulty in ionizing when they once get the energy, because of their more rapid gain of energy in the field. At this point the exponential rise of α/p ceases, and, as the rate of energy gain increases, the decreased ionizing efficiency with increasing energy causes a cessation in the rate of increase in α/p, so that α/p tends towards a more constant value. A more accurate discussion is hardly possible, as the mathematical difficulties introduced into theory by inelastic impacts at low energies, attachment, radiation losses, the probability of ioniza-

tion and radiation as a function of energy, and finally the variable electron mean free paths are practically unsurmountable. Hence it is seen that here again kinetic-theory analysis falls short of achievement because of its complexity. Enough, however, has been gained from this analysis to show again the usefulness of the kinetic-theory analysis in giving an order-of-magnitude insight into the nature of the phenomenon.

References

1. For most of the facts stated in the introduction the following references may be consulted:
   a. Crowther, J. A.: "Ions, Electrons and Ionizing Radiations," Chaps. I–V, VIII, IX, Edward Arnold & Co., London, 1924.
   b. Przibram, K.: "Handbuch der Physik," vol. 22, p. 307 ff., Julius Springer, Berlin, 1925; 2d ed., Chap. IV, p. 343, 1932.
   c. Bloch, L.: "Ionisation et Résonance des Gaz et des Vapeurs," Chaps. I, II, Société Française de Physique, Paris, 1925.
   d. Thomson, J. J.: "Conduction of Electricity through Gases," 3d ed., vol. I, 1928, vol. II, 1933, Cambridge University Press, Cambridge.
   e. Townsend, J. S.: "Electricity in Gases," Oxford University Press, Oxford, 1914.
   f. Franck, J.: Bericht über Ionenbeweglichkeit, *Jahrb. Radioakt. Electronik*, **9,** 248, 1912.
   g. Darrow, K. K.: "Electrical Phenomena in Gases," Williams & Wilkins Co., Baltimore, 1932.
   h. Compton and Langmuir: *Rev. Mod. Phys.*, **2,** 123–241, 1930; **3,** 191–258, 1931.
2. Loeb: *Phys. Rev.*, **19,** 24, 1922.
3. Compton, K. T.: *Phys. Rev.*, **22,** 333, 432, 1923.
4. Loeb: *Phys. Rev.*, **25,** 101, 1925.
5. Przibram: *Loc. cit.*, p. 329.
6. Nolan, J. J.: *Proc. Roy. Irish Acad.*, **A34,** 74, 1923.
7. Tyndall and Grindley: *Proc. Roy. Soc.*, **A110,** 341, 1926.
8. Wellisch: *Phil. Mag.*, **34,** 55, 1917.
9. Loeb: *Phys. Rev.*, **17,** 89, 1921.
10. Erikson: *Phys. Rev.*, **6,** 349, 1915.
11. Loeb: *Proc. Nat. Acad. Sci.*, **12,** 35, 42, 617, 680, 1926.
12. Millikan, R. A.: "The Electron," Chap. VI, Chicago University Press, Chicago, 1917.
13. Erikson, H. A.: *Phys. Rev.*, **20,** 117, 1922; **24,** 502, 1924; **26,** 465, 625, 629, 1925; **30,** 339, 1927.
14. Erikson: *Phys. Rev.*, **28,** 372, 1926; **24,** 622, 1924; **26,** 5, 1925.
15. Townsend: *Loc. cit.*, p. 174.
16. Thomson, J. J.: *Phil. Mag.*, **30,** 321, 1915.
17. Loeb: *Phil. Mag.*, **43,** 230, 1922; *Phys. Rev.*, **17,** 89, 1921.
18. Bailey: *Phil. Mag.*, **50,** 843, 1925.
19. Townsend: *Loc. cit.*, Chap. VIII.

20. Langevin: *Ann. Chim. Phys.*, **5,** 245, 1905; **28,** 317, 495, 1903.
21. Mayer, H. F.: *Ann. Physik*, **62,** 358, 1920.
22. Blackwood: *Phys. Rev.*, **16,** 85, 1920; **20,** 499, 1922.
23. Loeb: *J. Franklin Inst.*, **196,** 537, 1923.
24. Wellisch: *Phil. Trans.*, **A209,** 249, 1909.
25. Sutherland: *Phil. Mag.*, **18,** 341, 1909.
26. Compton and Langmuir: *Rev. Mod. Phys.*, **2,** 204–218, 1930.
27. Debye: Marx's "Handbuch der Radiologie," vol. 6, p. 605 ff.
28. Thomson, J. J.: *Phil. Mag.*, **47,** 337, 1924.
29. Loeb: *Phil. Mag.*, **48,** 446, 1924; **49,** 517, 1925.
30. Loeb, L. B.: *J. Franklin Inst.*, **201,** 279, 1926.
31. Langevin: *Ann. Chim. Phys.*, **8,** 238, 1905.
32. Loeb: *J. Franklin Inst.*, **184,** 775, 1917.
33. Hassé and Cook, *Phil. Mag.*, **12,** 554, 1931.
34. Loeb and Marshall: *J. Franklin Inst.*, **208,** 371, 1929.
35. Blanc: *J. Physique*, **7,** 825, 1908.
36. Loeb and Ashley: *Proc. Nat. Acad. Sci.*, **10,** 351, 1924.
37. Plimpton, S. J.: *Phil. Mag.*, **25,** 65, 1913.
38. Kovarick: *Phys. Rev.*, **30,** 443, 1910.
39. Phillips: *Proc. Roy. Soc.*, **A73,** 167, 1900.
40. Hassé: *Phil. Mag.*, **1,** 139, 1926.
41. Marshall, L. C.: *Phys. Rev.*, **34,** 618, 1929.
42. Bragg: "Studies in Radioactivity," Chap. VII, p. 67, Macmillan & Co., Ltd., London, 1912.
43. Langevin: *Ann. Chim. Phys.*, **28,** 433, 1903.
44. Richardson: *Phil. Mag.*, **10,** 242, 1905.
45. Thomson, J. J.: *Phil. Mag.*, **47,** 337, 1924.
46. Thirkill: *Proc. Roy. Soc.*, **A88,** 490, 1913.
47. Loeb, L. B.: *Trans. Am. Electrochem. Soc.*, **60,** 131, 1929.
48. Erikson: *Phil. Mag.*, **18,** 328, 1909.
49. Townsend: *Phil. Trans. Roy. Soc.*, **A193,** 157, 1900.
50. Rümelin: *Ann. Physik*, **43,** 852, 1913.
51. Wahlin: *Phys. Rev.*, **19,** 173, 1922.
52. Franck and Hertz: *Verh. Deut. Phys. Ges.*, **15,** 373, 613, 1913.
53. Compton and Benade: *Phys. Rev.*, **9,** 187, 1918.
54. Townsend and Tizzard: *Proc. Roy. Soc.*, **A87,** 357, 1912; **A88,** 336, 1913; *Phil. Mag.*, **42,** 874, 1921; **44,** 1033, 1922; **46,** 657, 1923. Skinker and White: *Phil. Mag.*, **46,** 630, 1923.
55. Wahlin: *Phys. Rev.*, **23,** 169, 1924.
56. Wellisch: *Am. J. Sci.*, **44,** 1, 1917.
57. Franck: *Verh. Deut. Phys. Ges.*, **12,** 291; 613, 1910.
58. Lewis, G. N.: "Valence and Structure of the Atom," Monograph Series, American Chemical Society, 1923.
59. Loeb: *J. Franklin Inst.*, **197,** 45, 1924.
60. Compton and Mohler: *Bull. Nat. Research Council*, vol. 9, No. 48, 1924.
61. Compton: *Phys. Rev.*, **7,** 489, 502, 1916.
62. Hughes and Klein: *Phys. Rev.*, **23,** 111, 450, 1924.
63. Compton and Van Voorhis: *Phys. Rev.*, **26,** 436, 1925.
64. Lawrence: *Phys. Rev.*, **27,** 515, 809, 1926.

65. Sponer: *Z. Physik*, **7**, 185, 1921.
66. Bradbury, N. E.: *Phys. Rev.*, **40**, 508, 524, 1932.
67. Compton and Langmuir: *Rev. Mod. Phys.*, **2**, 219, 1930.
68. Bradbury, N. E.: *Phys. Rev.*, **37**, 1311, 1931.
69. Loeb and Bradbury: *Phys. Rev.*, **38**, 1716, 1931.
70. Zeleny, John: *Phys. Rev.*, **34**, 310, 1929; **36**, 35, 1930.
71. Loeb, L. B.: *Phys. Rev.*, **32**, 81, 1928.
72. Loeb, L. B.: *Science*, **67**, 468, 1928. Loeb and Loeb: *Proc. Nat. Acad. Sci.*, **15**, 305, 1929.
73. Cravath, A. M.: *Phys. Rev.*, **33**, 605, 1929.
74. Bradbury, N. E.: *Phys. Rev.*, **44**, 883, 1933.
75. Bradbury, N. E.: *Phys. Rev.*, **40**, 980, 1932.
76. Loeb and Dyk: *Proc. Nat. Acad. Sci.*, **15**, 146, 1929. Loeb, L. B.: *Phys. Rev.*, **35**, 184, 1930. Loeb, L. B.: *Z. Physik*, **75**, 555, 1932. Tyndall and Phillips: *Proc. Roy. Soc.*, **A111**, 577, 1926.
77. Loeb, L. B.: *Phys. Rev.*, **38**, 549, 1931.
78. Tyndall and Powell: *Proc. Roy. Soc.*, **A129**, 162, 1930; **A134**, 125, 1931; **A136**, 145, 1932.
79. Powell and Brata: *Proc. Roy. Soc.*, **A138**, 117, 1933.
80. Luhr, O.: *Phys. Rev.*, **38**, 1730, 1931; *Phys. Rev.*, **44**, 459, 1933.
81. Kallmann and Rosen: *Z. Physik*, **58**, 52, 1929; **61**, 61, 1930; **64**, 806, 1930.
82. Loeb, L. B.: *Phys. Rev.*, **8**, 633, 1916. Yen, K. L.: *Phys. Rev.*, **9**, 337, 1918.
83. Harper, W. R.: *Proc. Cambridge Phil. Soc.*, **28** (Part II), 219, 1932.
84. Luhr, O.: *Phys. Rev.*, **35**, 1394, 1930; **36**, 24, 1930. Luhr and Bradbury: *Phys. Rev.*, **36**, 998, 1931.
85. Kenty, C.: *Phys. Rev.*, **32**, 624, 1928.
86. Cravath, A. M.: *Phys. Rev.*, **36**, 248, 1930.
87. Ruark and Urey, "Atoms, Molecules and Quanta," pp. 392–403, McGraw-Hill Book Company, Inc., New York, 1930. Franck and Jordan: "Anregung von Quantensprüngen durch Stösse," p. 275 ff., Julius Springer, Berlin, 1926.
88. Baerwald, H.: *Phys. Z.*, **26**, 868, 1925.
89. Harries, W.: *Z. Physik*, **42**, 26, 1927.
90. Loeb, L. B.: *Phil. Mag.*, **8**, 98, 1929.
91. Thomson, J. J.: "Conduction of Electricity through Gases," 3d ed., p. 466, Cambridge University Press, Cambridge, 1928.
92. Davis, Bergen: *Phys. Rev.*, **24**, 93, 1907; **5**, 118, 1915.
93. Sanders, F. H.: *Phys. Rev.*, **41**, 667, 1932; **44**, 1020, 1933.
94. Paavola: *Archiv. Elektrotechnik*, **22**, 473, 1929.
95. Masch, K.: *Archiv. Elektrotechnik*, **26**, 587, 1932.

Books Recommended

See Reference 1, in references to Chap. XI.

APPENDIX I

DIAMETERS OF MOLECULES

The term originates from the original picture of molecules as hard elastic spheres (see Secs. 13 and 14). If two such identical molecular spheres are placed so that they are in contact, the diameter would be defined as the distance between their centers. The contact between the spheres, on such a picture, is defined as the closest approach of the centers on an average impact. The diameter in a solid would be defined as the distance between the centers at equilibrium for molecules arranged in a solid space lattice. This picture, which was adequate until the discovery of the electron, still determines our mode of description in the kinetic theory because of its simplicity.

Actually, molecules are known today to consist of nuclei of positive electricity surrounded by planetary electrons with orbital motions. It is obvious that such configurations of electrical charges cannot be considered hard elastic spheres in the old sense of the term. What really affect the motions of the molecules and atoms are the electrical fields of force between the electrons and nuclei of the atomic configurations. In general, such force fields, with the possible exception of those about the heavier inert gas atoms, are probably force fields with equipotential surfaces which are far from spherical, although perhaps symmetrical about their axes. The force fields are, in general, composed of two sets of forces, forces of attraction of small magnitude varying slowly with the distance (the cohesive forces, or those responsible for Van der Waals' a), and repulsive forces of considerable magnitude which fall off very much more rapidly with the distance (the elastic repulsive forces of the old kinetic-theory molecules). How such opposing forces can occur simultaneously in the atoms is briefly discussed in Sec. 52. The rate at which the force varies with the distance from the atomic centers has been estimated from the crystal structure of sodium chloride by Born to be proportional to the inverse ninth power of the distance. The work of Lennard Jones, based on the

study of gases, gives the repulsive forces as lying between an inverse ninth power and an inverse fifteenth power, while the attractive forces lie between forces varying inversely as the fourth power and inversely as the sixth power.

With atoms and molecules of such a nature, the meaning of the term "diameter" must be modified or at least one must understand the application of the term to such a picture. Measurements of molecular diameters are made in all cases on a *very large number of individuals.* In all cases for gases they are made for individuals *oriented in all possible directions.* Finally, in the case of gases, the conditions of impact due to velocity distribution will influence the distance of approach; and one must deal with *an average value. It is possible, therefore, to couch the experimental conclusions in terms of the very simple picture of elastic spheres of a given diameter, the diameter in such a case being the statistical average distance of approach of the molecules for the average velocity.* An analysis expressed in terms of such a picture is entirely justified, as it influences the results but little, while it simplifies calculation and interpretation greatly. When such pictures are used, however, one must remember that they are conveniences and that the actual molecules may be entirely different in appearance. Even in the case of crystal analysis, the investigators find it convenient to express atomic diameters in terms of the elastic sphere.*

On the other hand, it must be clear that the values of the average diameters which are obtained for atoms and molecules from different types of investigation will not necessarily agree accurately in value, though the measurements may, in general, agree in order of magnitude. That this must be so can be clearly seen, for in a crystal two atoms are bound together by forces of electrical attraction. The average distance at which these atoms are held in equilibrium is determined by the repulsive forces as well. On the other hand, in the gaseous state, where the attractive forces may be quite different owing to the absence of closely surrounding atoms and where the velocities of agitation may be very different, the average distance of approach on an impact will not be the same as the average distance between centers in the crystal. It is also clear that the more violent the impact because of higher temperatures, the smaller will be the apparent diameter. A particular case where the results would be expected to vary from other results obtained is in the case of

* Bragg, W. L., *Phil. Mag.*, **40**, 169, 1920.

the measurement of the diameter of a molecule by the impact with electrons. The average distance of approach for an impact will be determined by the ease with which the electron is deflected from its straight-line path. It will depend on the action of the atomic field of force, and on the motion of the electron. This depends on the time integral of the force and will obviously be less, the faster the electron is moving. Again, with such a minute body as the electron, the distance of approach before deflection will depend upon the portion of the atom struck. Finally, it seems probable that for electrons of a certain speed, there will be a possible interaction on the electron when its velocity in passing the atom is of the order of magnitude of the orbital velocities of electrons in the atom itself. Such effects have actually been observed. Finally, it has also been observed that electrons, moving with an extremely slow velocity in the case of certain atoms, can pass right through them without change of energy or direction (see Sec. 25). It is thus obvious that the molecular diameter, as measured by the electron, may vary through enormous ranges; and, *in comparing results of measurements on atomic or molecular diameters, one must always bear in mind that they may represent really very different things.* The conclusion is that the term "atomic or molecular diameter" has a meaning in more than order of magnitude, *only when spoken of in terms of its method of measurement.* The discussion which has preceded forms, therefore, a fitting introduction to a comparative table of molecular diameters which is given below, together with the method of measurement yielding the results.

The methods by which molecular dimensions have been obtained may be seen summarized below, as given by K. F. Hertzfeld:*

I. Measurements based on the equation of state.
  1. Calculation from critical data.
  2. From volumes below the critical.
  3. Calculation from gas isotherms.
  4. Crystal structure.
    a. Spherical packing.
    b. Permutite.
    c. True dimensions.

II. Methods involving a dynamical study.
  1. In gases.
    a. Deflection of electrons.
    b. Direct measurement of free paths of atoms.
    c. Coefficient of viscosity.

* Hertzfeld, K. F., *Jahrbuch der Radioaktivität und Elektronik*, **19**, 259, 1922.

2. In liquids.
   a. From Stokes' law.
   b. Viscosity in liquids.
      (1) Theory of viscosity.
      (2) Increase of viscosity in solutions.
   c. Diffusion of neutral particles.
   d. Ionic mobilities.

III. Energy methods.
   1. Heat of hydration.
   2. Ionizing potential.
   3. Heat of vaporization.
   4. Melting point.

IV. Method of thin films.
   1. Determination of the number of molecules per unit area in a monomolecular layer.
   2. Optical determination of thickness of films.
   3. Electrical determination of thickness of films.

V. Optical methods.
   1. Determination of true ionic size with X-rays.
   2. Molecular refraction.

VI. Determination of the size of electronic orbits in atoms.
   1. Diamagnetic properties.
   2. Calculation from atomic models.

VII. Methods for determination of moments of inertia and electrical moments. (Such measurements give the distance between the nuclei in molecules and the distance between the apparent separation of positive and negative electricity considered as point charges necessary to produce the effects. They are not necessarily true measures of molecular diameter in the sense of the kinetic theory.)

In papers, J. E. Lennard Jones* gives the following values of the attractive and repulsive forces in the following gases as most successfully fitting the data. In all cases, the *attractive* force seeming to be the most suitable *is an inverse fifth power law.* For the *repulsive* forces in the following gases, the law *varies inversely* with the power of the distance indicated under the letter n for the respective gas:

Gas	n
He	9, 11, 14
Ne	11
Ar	9
Kr	10
Xe	11
H_2	11
N_2	9, 11, 14

* Lennard Jones, J. E., *Proc. Roy. Soc.*, **A-106,** 441, 463, 709, 1924; and **A-112,** 214, 230, 1926.

Radii of Molecules

Determined by Various Methods, Radii Are All Given in 10^{-8} Cm.

Method	He	Ne	Ar	Kr	X	Hg	H_2	N_2	O_2
From $b = \frac{1}{8}\frac{RT_K}{p_K}$ (Van der Waals)	1.15	.....	1.43						❶
	1.321	.....	1.437	1.57	1.71	1.186	1.380	1.573	1.453
From $b = \frac{1}{15}\frac{RT_K}{p_K}$ (Wohl)	1.071	.....	1.165	1.27	1.39	0.962	1.119	1.276	1.178
*Tetrahedral packing in liquids	3.17	.....	3.20	3.55	3.51	2.58	3.15	3.35	3.08
Gas isotherms	Temp. −271.5°	.....	Temp. −189°	Temp. −146°	Temp. −102°	Temp. −39°	Temp. −258°	Temp. −202°	Temp. −227°
	1.39 Temp. 0°								
	1.12 Temp. 293°	.....	1.21 Temp. 0°	.....	.....	.....	1.16	1.49	1.325
Slow-moving electrons	1.41	1.275	2.77	.....	.....	.....	2.04	1.75	
						1.78			
Viscosity	.....	1.17	1.43	1.59	1.75	1.82	1.088	1.58	1.48
Molecular refraction	0.741	0.922	1.48	1.666	2.002	.....	0.929	1.20	1.169
Diamagnetism	.....	.....	.....	.....	.....	0.55	1.46	0.76	0.65
Molecular distance from Band spectra	.....	.....	.....	.....	.....	.....	2×0.25	.....	2×0.56
Molecular distance from Chemical constants	.....	.....	.....	.....	.....	.....	2×0.26	.....	2×0.77
							2×0.18	2×0.97	2×1.35
Dipolar distance									

Method	Cl_2	Br_2	I_2	$(CN)_2$	HF	HCl	HBr	CO	CO_2	H_2O
From $b = \frac{1}{8}\frac{RT_K}{p_K}$ (Van der Waals)	1.654	.....	....	1.893	.....	1.590	.....	2.276	1.614	1.443
From $b = \frac{1}{15}\frac{RT_K}{p_K}$ (Wohl)	1.341	.....	....	1.545	.....	1.290	.....	1.844	1.309	1.170
Tetrahedral packing in liquids	3.68	3.90	....	.....	2.84	3.31	3.52	3.37	3.65	2.74
Gas isotherms	Temp. −80°	Temp. −4°	....	.....	Temp. +13°	Temp. −83°	Temp. −65°	Temp. −205°	Temp. −34°	Temp. +4°
Slow-moving electrons	.....	.....	.....	.....	.....	.....	.....	.....	1.83	
Viscosity	1.85	2.02	2.23	2.04	.....	.....	.....	.....	.....	1.36
Molecular refraction	1.647	1.859	....	.....	.....	1.368	1.517	.....	.....	1.130
Diamagnetism	0.92									
Molecular distance from Band spectra	.....	.....	....	.....	.....	1.34	1.49	1.14		
Molecular distance from Chemical constants					0.924	1.276	1.419			
	.....	.....	....	.....	.....	.....	.....	0.94		
Dipolar distance	.....	.....	....	.....	.....	.....	.....	0.025	0.0075	0.2

* Due to an error the results here are all too high by a factor of $\sqrt[3]{4}$

APPENDIX II

FUNDAMENTAL PHYSICAL CONSTANTS*

TABLE A.—PRINCIPAL CONSTANTS AND RATIOS

Velocity of light ..... c = $(2.99796 \pm 0.00004) \times 10^{10}$ cm · sec^{-1}
Gravitation constant ..... G = $(6.64 \pm 0.002) \times 10^{-8}$ dyne · cm^2 · g^{-2}
Liter ..... l = 1000.027 ± 0.001 cm^3
Volume of perfect gas (0°C, A_n) ..... v_n = $(22.4141 \pm 0.0008) \times 10^3$ cm^3 · mole^{-1}
R_n = 22.4135 ± 0.0008 liter · mole^{-1}
Volume of perfect gas (0°C, A_{45}) .... R = 22.4146 ± 0.0008 liter · mole^{-1}
International ohm (= p abs-ohm) ... p = 1.00051 ± 0.00002
International ampere (= q abs-amp) q = 0.99995 ± 0.00005

Atomic weights

O (oxygen)	= 16.0000 (definition)	Ag (silver)	= 107.880 ± 0.001
H (hydrogen)	= 1.00777 ± 0.00002	I (iodine)	= 126.932 ± 0.002
He (helium)	= 4.0022 ± 0.0004	C (carbon)	= 12.003 ± 0.001
N (nitrogen)	= 14.0083 ± 0.0008	Ca (calcium)	= 40.075 ± 0.005

Normal atmosphere ..... A_n = $(1.013249 \pm 0.000003) \times 10^6$ dyne · cm^{-2}
45° atmosphere ..... A_{45} = $(1.013199 \pm 0.000003) \times 10^6$ dyne · cm^{-2}
Ice point (absolute scale) ..... T_0 = 273.18 ± 0.03°K
Mechanical equivalent of heat ..... J_{15} = 4.1852 ± 0.0006 abs-joule · cal$_{15}^{-1}$
J_{20} = 4.1813 ± 0.0006 abs-joule · cal$_{20}^{-1}$
Electrical equivalent of heat ..... J'_{15} = 4.1835 ± 0.0007 int-joule · cal$_{15}^{-1}$
J'_{20} = 4.1796 ± 0.0007 int-joule · cal$_{20}^{-1}$
Faraday constant ..... F = 96494 ± 5 int-coul · g-equiv^{-1}
= 96489 ± 7 abs-coul · g-equiv^{-1}
= 9648.9 ± 0.7 abs-*em*-unit · g-equiv^{-1}
Fc = $(2.8927_0 \pm 0.0002) \times 10^{14}$ abs-*es*-unit · g-equiv^{-1}
Electronic charge ..... e = $(4.770 \pm 0.005) \times 10^{-10}$ abs-*es*-units
e/c = $(1.5910_8 \pm 0.0016) \times 10^{-20}$ abs-*em*-units
Specific electronic charge (spectroscopic) ..... e/m = $(1.761 \pm 0.001) \times 10^7$ abs-*em*-unit · g^{-1}
$(e/m)c$ = $(5.279_{41} \pm 0.003) \times 10^{17}$ abs-*es*-unit · g^{-1}
Specific electronic charge (deflection) ..... e/m = $(1.769 \pm 0.002) \times 10^7$ abs-*em*-unit · g^{-1}
$(e/m)c$ = $(5.303_{39} \pm 0.006) \times 10^{17}$ abs-*es*-unit · g^{-1}
Planck constant ..... h = $(6.547 \pm 0.008) \times 10^{-27}$ erg · sec

TABLE B.—ADDITIONAL QUANTITIES EVALUATED OR USED IN CONNECTION WITH TABLE A

Ratio of *es* to *em* units (direct) ..... c' = $(2.9971 \pm 0.0001) \times 10^{10}$ cm$^{1/2}$ · sec$^{-1/2}$ · int $\Omega^{-1/2}$
= $(2.9979 \pm 0.0001) \times 10^{10}$ cm · sec^{-1}
Ratio of *es* to *em* units (indirect) $c' = c$ = $(2.99796 \pm 0.00004) \times 10^{10}$ cm · sec^{-1}
Acceleration of gravity (45°) ..... g_{45} = 980.616 cm · sec^{-2}
Mean density of earth ..... δ = 5.522 ± 0.002 g · cm^{-3}
Maximum density of water ..... δ_m = 0.999973 ± 0.000001 g · cm^{-3}
Acceleration of gravity (normal) .... g_n = 980.665 cm · sec^{-2}
Density of oxygen gas (0°C, A_{45}) .... L = 1.428965 ± 0.000030 g · liter^{-1}

* From an article by R. T. Birge, *Rev. Mod. Phys.*, **1**, 1, 1929, through the courtesy of the American Institute of Physics.

Factor converting oxygen (0°C, A_{46}) to ideal gas ..... $1 - \alpha$	= 1.000927 ± 0.000030
International coulomb (= q abs-coul) . q	= 0.99995 ± 0.00005
International henry (= p abs-henry) . . p	= 1.00051 ± 0.00002
International volt (= pq abs-volt) . pq	= 1.00046 ± 0.00005
International joule (= pq^2 abs-joule) . ..... pq^2	= 1.00041 ± 0.00010
International gauss (= q abs-gauss)	
Density of nitrogen (0°C, A_{46}) L	= 1.25046 ± 0.000045 g · liter^{-1}
Factor converting nitrogen (0°C, A_{46}) to ideal gas ..... $1 - \alpha$	= 1.00043 ± 0.00002
Specific gravity of Hg (0°C, A_n) referred to air-free water at maximum density ..... ρ_n	= 13.59546 ± 0.00003
Density of Hg (0°C, A_n) ..... D_n	= 13.59509 ± 0.00003 g · cm^{-3}
Electrochemical equivalent of silver E_{Ag}	= (1.11800 ± 0.00005) × 10^{-3} g · int-coul^{-1}
	= (1.11805 ± 0.00007) × 10^{-3} g · abs-coul^{-1}
Arbitrary calcite grating space (18°C) ..... d_{18}''	= 3.02904 × 10^{-8} cm
Density of calcite (20°C) ..... ρ	= 2.7102 ± 0.0004 g · cm^{-3}
Structural constant of calcite (20°C) ..... $\phi(\beta)$	= 1.09630 ± 0.00007
Rydberg constant for hydrogen .... R_H	= 109677.759 ± 0.05 cm^{-1}
Rydberg constant for ionized helium .... R_{He}	= 109722.403 ± 0.05 cm^{-1}
Wave-length of red Cd line (15°C, A_n) ..... λ(Cd)	= 6438.4696 I.A. (definition of I.A. unit)
Rydberg constant for infinite mass . . R_∞	= 109737.42 ± 0.06 cm^{-1}
$R_\infty c$	= (3.28988 ± 0.00004) × 10^{15} sec^{-1}
R_∞ (indirect) = $2\pi^2 e^5/h^3c^2(e/m)_{sp}$	= 109734 ± 170 cm^{-1}
$R_\infty c$ (indirect)	= (3.290$_{08}$ ± 0.005) × 10^{15} sec^{-1}
e/m (spectroscopic, indirect)	
$e/m = 2\pi^2 e^5/h^3c^2R_\infty$	= (1.7611$_2$ ± 0.0025) × 10^7 abs-em-unit · g^{-1}
True grating space of calcite (20°C) . d'_{20}	= (3.0283 ± 0.0010) × 10^{-8} cm
Effective grating space of calcite (20°C) ..... d_{20}	= (3.0279 ± 0.0010) × 10^{-8} cm
Avogadro's number ..... $N_0 = Fc/e$	= (6.064$_{36}$ ± 0.006) × 10^{23} mole^{-1}
Gas constant per mole . . $R_0 = \nu_n A_n/T_0$	= (8.3136$_0$ ± 0.0010) × 10^7 erg · deg^{-1} · mole^{-1}
$R_0' = R_0/(J_{15} \times 10^7)$	= 1.9864$_3$ ± 0.0004 cal$_{15}$ · deg^{-1} · mole^{-1}
$R_0'' = R_0/A_n \times 1000.027)$	= (8.2046$_4$ ± 0.0009) × 10^{-2} liter · atmos · deg^{-1} · mole^{-1}
$R_0''' = R_0/A_n = \nu_n/T_0$	= 82.048$_8$ ± 0.009 cm^3 · atmos · deg^{-1} · mole^{-1}
Boltzmann constant ..... $k = R_0/N_0$	= (1.3708$_8$ ± 0.0014) × 10^{-16} erg · deg^{-1}
Second radiation constant (experimental) ..... c_2	= 1.432 ± 0.003 cm · deg
Second radiation constant (indirect) ..... $c_2 = hc/k$	= 1.4317$_4$ ± 0.0006 cm · deg
Stefan-Boltzmann constant (experimental) ..... σ	= (5.735 ± 0.011) × 10^{-5} erg · cm^{-2} · deg^{-4} · sec^{-1}
Stefan-Boltzmann constant (indirect ..... $\sigma = 2\pi^5 k^4/15c^2h^3$	= (5.713$_9$ ± 0.006) × 10^{-5} erg · cm^{-2} · deg^{-4} · sec^{-1}
Radiation density constant (experimental) ..... $a = 4\sigma/c$	= (7.651$_8$ ± 0.015) × 10^{-15} erg · cm^{-3} · deg^{-4}
Radiation density constant (indirect) ..... $a = 8\pi^5 k^4/15c^3h^3$	= (7.623$_7$ ± 0.007) × 10^{-15} erg · cm^{-3} · deg^{-4}

TABLE C.—MISCELLANEOUS DERIVED CONSTANTS

$c^2 = (8.98776 \pm 0.00024) \times 10^{20}$ cm$^2 \cdot$ sec^{-2}	$h/c = (2.183_{81} \pm 0.003) \times 10^{-37}$ g $\cdot$ cm
$c^3 = (26.9449 \pm 0.0011) \times 10^{30}$ cm$^3 \cdot$ sec^{-3}	$e^2 = (22.752_9 \pm 0.045) \times 10^{-20}$ *es*-units^2
$c^4 = (80.7798 \pm 0.0043) \times 10^{40}$ cm$^4 \cdot$ sec^{-4}	$e^3 = (108.53_{13} \pm 0.33) \times 10^{-30}$ *es*-units^3
$h^2 = (42.863 \pm 0.10) \times 10^{-54}$ erg$^2 \cdot$ sec^2	$e^4 = (517.6_{94} \pm 2.1) \times 10^{-40}$ *es*-units^4
$h^3 = (280.6_{25} \pm 1.0) \times 10^{-81}$ erg$^3 \cdot$ sec^3	$e^5 = (2469._{40} \pm 12) \times 10^{-50}$ *es*-units^5

Mass of electron (spectroscopic) $\ldots\ldots m_0 = \dfrac{e}{c(e/m)_{sp}} = (9.035_{10} \pm 0.010) \times 10^{-28}$ g

Mass of electron (deflection) $\ldots\ldots m_0 = \dfrac{e}{c(e/m)_{defl}} = (8.\dot{9}94_{25} \pm 0.014) \times 10^{-28}$ g

Atomic weight of electron (spectroscopic) $\ldots\ldots m = F/(e/m)_{sp} = (5.479_{22} \pm 0.003) \times 10^{-4}$

Atomic weight of electron (deflection) $\ldots\ldots m = F/(e/m)_{defl} = (5.454_{44} \pm 0.006) \times 10^{-4}$

Mass of atom of unit atomic weight $\ldots\ldots M_0 = 1/N_0 = (1.6489_8 \pm 0.0016) \times 10^{-24}$ g

Mass of hydrogen atom $\ldots\ldots M_H = H/N_0 = (1.6617_9 \pm 0.0017) \times 10^{-24}$ g

Atoms per gram of hydrogen $\ldots\ldots 1/M_H = (6.017_{61} \pm 0.006) \times 10^{23}$ g^{-1}

Mass of proton $\ldots\ldots M_P = (H - m)/N_0 = (1.6608_9 \pm 0.0017) \times 10^{-24}$ g

Mass of α particle $\ldots\ldots M_\alpha = (He - 2m)/N_0 = (6.597_{74} \pm 0.007) \times 10^{-24}$ g

Charge in electrolysis of 1 g hydrogen $\ldots\ldots e/M_H = F/H = 9574.5_1 \pm 0.7$ abs-*em*-units $\cdot$ g^{-1}

Specific charge of proton $\ldots\ldots e/M_P = F/(H - m) = 9579.7_3 \pm 0.7$ abs-*em*-units $\cdot$ g^{-1}

Specific charge of α particle $\ldots\ldots 2e/M_\alpha = 2F/(He - 2m) = 4823.1_1 \pm 0.6$ abs-*em*-units $\cdot$ g^{-1}

Ratio mass H atom to mass electron (spectroscopic) $\ldots\ldots \dfrac{(e/m)_{sp}}{e/M_H} = 1839._{26} \pm 1$

Ratio mass H atom to mass electron (deflection) $\ldots\ldots \dfrac{(e/m)_{defl}}{e/M_H} = 1847._{61} \pm 2$

Ratio mass proton to mass electron (spectroscopic)

$= 1839.26 - 1 = 1838._{26} \pm 1$

Ratio mass proton to mass electron (deflection) $= 1847.61 - 1 = 1846._{61} \pm 2$

TABLE C.—MISCELLANEOUS DERIVED CONSTANTS—(*Continued*)

Energy associated with unit wave-number	$\epsilon/\nu' = hc$	$= (1.9627_{64} \pm 0.0025) \times 10^{-16}$ erg · cm
Potential associated with unit frequency	$V/\nu = h/e$	$= (1.3725_4 \pm 0.0005) \times 10^{-17}$ erg · sec · *es*-unit^{-1}
Frequency associated with unit potential	$\nu/V = e/h$	$= (7.2857_7 \pm 0.0027) \times 10^{16}$ *es*-unit · erg^{-1} · sec^{-1}
	$\nu/V'' = e \cdot 10^8/hc$	$= (2.4302_5 \pm 0.0009) \times 10^{14}$ sec^{-1} · abs-volt^{-1}
Wave-number associated with 1 abs-volt		
	$\nu_0 = \nu'/V'' = e \cdot 10^8/hc^2$	$= 8106._{31} \pm 3$ cm^{-1} · abs-volt^{-1}
Wave length associated with 1 abs-volt	$\lambda_0 = \lambda V'' = hc^2/e$	$= (12336._1 \pm 5) \times 10^{-8}$ cm · abs-volt
Energy of 1-abs-volt-electron	$h\nu/V'' = e \cdot 10^8/c$	$= (1.5910_8 \pm 0.0016) \times 10^{-12}$ erg
Speed of 1-abs-volt-electron (spectroscopic)		
	$v_e = [2 \cdot 10^8 (e/m)_{sp}]^{1/2}$	$= (5.9346_4 \pm 0.0017) \times 10^7$ cm · sec^{-1}
Speed of 1-abs-volt-electron (deflection)	$v_e = [2 \cdot 10^8 (e/m)_{defl}]^{1/2}$	$= (5.9481_1 \pm 0.0034) \times 10^7$ cm · sec^{-1}
Fine structure constant	$\alpha = 2\pi e^2/hc$	$= (7.283_{64} \pm 0.006) \times 10^{-3}$
Reciprocal of fine-structure constant	$1/\alpha$	$= 137.29_4 \pm 0.11$
Square of fine-structure constant	α^2	$= (5.305_{13} \pm 0.008) \times 10^{-5}$
Bohr unit of angular momentum	$h/2\pi$	$= (1.0419_9 \pm 0.0013) \times 10^{-27}$ erg · sec
	$e^2/c = \alpha h/2\pi$	$= (7.589_{46} \pm 0.015) \times 10^{-30}$ *es*-unit^2 · sec · cm^{-1}
Magnetic moment of 1 Bohr magneton (spectroscopic)		
	$\mu_1 = (h/4\pi)(e/m)_{sp}$	$= (0.9174_{70} \pm 0.0013) \times 10^{-20}$ erg · gauss^{-1}
Magnetic moment of 1 Bohr magneton (deflection)		
	$\mu_1 = (h/4\pi)(e/m)_{defl}$	$= (0.9216_{38} \pm 0.0016) \times 10^{-20}$ erg · gauss^{-1}
Ratio Bohr magneton to Bohr mechanical unit (spectroscopic)		
	$\frac{\mu_1}{h/2\pi} = \frac{1}{2}\left(\frac{e}{m}\right)_{sp}$	$= 0.8805 \pm 0.0005) \times 10^7$ gauss^{-1} · sec^{-1}
Ratio Bohr magneton to Bohr mechanical unit (deflection)		
	$\frac{\mu_1}{h/2\pi} = \frac{1}{2}\left(\frac{e}{m}\right)_{defl}$	$= (0.8845 \pm 0.0010) \times 10^7$ gauss^{-1} · sec^{-1}

TABLE C.—MISCELLANEOUS DERIVED CONSTANTS—(*Continued*)

Magnetic moment per mole for one Bohr magneton per molecule (spectroscopic)

$$\mu_1 N_0 = 5563.87 \pm 10 \text{ ergs} \cdot \text{gauss}^{-1} \cdot \text{mole}^{-1}$$

Same (deflection) $\mu_1 N_0 = 5589.14 \pm 11 \text{ ergs} \cdot \text{gauss}^{-1} \cdot \text{mole}^{-1}$

Zeeman displacement per gauss $\frac{\Delta\nu'}{H} = \frac{(e/m)_{sp}}{4\pi c} = (4.674_{38} \pm 0.003) \times 10^{-5} \text{ cm}^{-1} \cdot \text{gauss}^{-1}$

Band-spectra constant connecting wave number and moment of inertia, I

$$h/8\pi^2 c = (27.65_{83} \pm 0.04) \times 10^{-40} \text{ g} \cdot \text{cm}$$

Same, connecting frequency and I $h/8\pi^2 = (8.291_{87} \pm 0.011) \times 10^{-29} \text{ erg} \cdot \text{sec}$

Same, connecting ergs and I $h^2/8\pi^2 = (5.428_{69} \pm 0.014) \times 10^{-55} \text{ erg}^2 \cdot \text{sec}^2$

Atomic specific heat constant $c_2/c = h/k = (4.7757_3 \pm 0.0019) \times 10^{-11} \text{ sec} \cdot \text{deg}$

Rotational specific heat constant $\sigma IT = h^2/8\pi^2 k = (39.59_{97} \pm 0.06) \times 10^{-40} \text{ g} \cdot \text{cm}^2 \cdot \text{deg}$

Reduced mass of H atom $\mu_H = R_H(m_0)_{sp}/R_\infty = (9.030_{19} \pm 0.010) \times 10^{-28} \text{ g}$

Schroedinger constant for H atom $8\pi^2\mu_H/h^2 = (1.663_{42} \pm 0.003) \times 10^{27} \text{ g} \cdot \text{erg}^{-2} \cdot \text{sec}^{-2}$

Schroedinger constant for electron $8\pi^2(m_0)_{sp}/h^2 = (1.664_{32} \pm 0.003) \times 10^{27} \text{ g} \cdot \text{erg}^{-2} \cdot \text{sec}^{-2}$

Ionization potential for H atom $R_H/\nu_0 = 13.529_9 \pm 0.005$ abs-volt

Ionization potential for He^+ $4R_{He}/\nu_0 = 54.141_7 \pm 0.020$ abs-volt

Separation of nucleus and electron in normal H atom, using experimental value of R_H

$$a_0 = \frac{\alpha(1-\alpha^2)^{1/2}}{4\pi R_H} = (0.5284_{56} \pm 0.0004) \times 10^{-8} \text{ cm}$$

Same, using calculated value of R_H $a_0 = \frac{h^2(1-\alpha^2)^{1/2}}{4\pi^2 e^2 \mu_H} = (0.5284_{21} \pm 0.0005) \times 10^{-8} \text{ cm}$

Radius of Bohr orbit in normal H, referred to center of mass, using experimental R_∞

$$a_0' = \frac{\alpha(1-\alpha^2)^{1/2}}{4\pi R_\infty} = (0.5281_{69} \pm 0.0004) \times 10^{-8} \text{ cm}$$

Same, using calculated R_∞ $a_0' = \frac{h^2 c(e/m)_{sp}(1-\alpha^2)^{1/2}}{4\pi^2 e^3} = (0.5281_{34} \pm 0.0005) \times 10^{-8} \text{ cm}$

TABLE C.—MISCELLANEOUS DERIVED CONSTANTS—(*Continued*)

Speed of electron in normal H orbit, referred to nucleus $v_0' = \alpha c$	$=$	$(2.1836_1 \pm 0.0017) \times 10^8$ cm · sec^{-1}
Same, referred to center of mass, using experimental R_H and R_∞		
$v_0 = \alpha c R_H/R_\infty$	$=$	$(2.1824_2 \pm 0.0017) \times 10^8$ cm · sec^{-1}
General spectroscopic doublet constant $R_\infty\alpha^2$	$=$	$5.821_{71} \pm 0.009$ cm^{-1}
Hydrogen doublet constant $\Delta\nu_H = R_H\alpha^2/16$	$=$	$0.3636_{59} \pm 0.0006$ cm^{-1}
Dispersion constant $e^2/2\pi m_0 = ec(e/m)_{sp}/2\pi$	$=$	$(4.007_{97} \pm 0.005) \times 10^7$ cm^3 · sec^{-2}
X-ray scattering coefficient $\frac{8\pi e^4}{3m_0^2c^4} = \frac{8\pi e^2(e/m)^2_{sp}}{3c^2}$	$=$	$(6.576_{91} \pm 0.015) \times 10^{-25}$ cm^2
Compton shift at 90° (spectroscopic) $\frac{h}{m_0c} = \frac{h}{e}\left(\frac{e}{m}\right)_{sp}$	$=$	$(0.024170_4 \pm 0.000016) \times 10^{-8}$ cm
Compton shift at 90° (deflection) $\frac{h}{m_0c} = \frac{h}{e}\left(\frac{e}{m}\right)_{defl}$	$=$	$(0.02428_{02} \pm 0.00003) \times 10^{-8}$ cm
Wave mechanics λ of 1-abs-volt-electron (spectroscopic) $\frac{h}{m_0(v_e)_{sp}}$	$=$	$(12.210_0 \pm 0.006) \times 10^{-8}$ cm
Loschmidt number (0°C, A_n) $n_0 = N_0/\nu_n$	$=$	$(2.705_{60}) \pm 0.003) \times 10^{19}$ cm^{-3}
Wien's displacement constant (indirect) $A = c_2/4.9651$	$=$	$0.28836_1 \pm 0.00011$ cm · deg
First radiation constant[1] $c_1 = 8\pi hc$	$=$	$(4.932_{96} \pm 0.006) \times 10^{-15}$ erg · cm
or hc^2	$=$	$(0.5884_{29} \pm 0.0008) \times 10^{-5}$ erg · cm^2 · sec^{-1}
or $2\pi hc^2$	$=$	$(3.697_{20} \pm 0.005) \times 10^{-5}$ erg · cm^2 · sec^{-1}

[1] Planck's radiation law is

$$E\lambda = \frac{c_1}{\lambda^5}\left(e^{-c_2/\lambda T} - 1\right)^{-1}$$

E_λ may be defined in various ways, and c_1 varies accordingly. If $E_\lambda d\lambda$ denotes the energy density of unpolarized radiation in range $d\lambda$, $c_1 = 8\pi hc$ (used by Coblentz and others). If $E_\lambda d\lambda$ denotes the intensity of emission of linearly polarized radiation in range $d\lambda$, perpendicular to a surface, per unit of surface, per unit solid angle, $c_1 = hc^2$ (Planck's own nomenclature, used generally in German texts). If $E_\lambda d\lambda$ denotes the emission of unpolarized radiation in range $d\lambda$, per unit surface, in all directions (2π solid angle), $c_1 = 2\pi hc^2$ (used in the "International Critical Tables" and elsewhere).

TABLE C.—MISCELLANEOUS DERIVED CONSTANTS—(*Concluded*)

Energy per mole for 1-abs-volt-electron per molecule		
$\frac{F \text{ (abs. coul per gram equiv.)}}{J_{15} \text{ (abs. joules per cal.)}}$		$= 23054.8 \pm 4$ $\text{cal}_{15} \cdot \text{mol}^{-1}$
Translational energy of molecule at 0°C	$E_0 = 3kT_0/2$	$= (5.617_{49} \pm 0.006) \times 10^{-14}$ erg
Translational energy per degree	$e_0 = E_0/T_0 = 3k/2$	$= (2.0563_3 \pm 0.0021) \times 10^{-16}$ erg $\cdot$ deg^{-1}
Sackur-Tetrode constant[2] (ϵ, base of ln = 2.71828)		
	$S_0 = R_0' \ln \frac{2\pi k^{3/2} \epsilon^{5/2}}{h^3 N_0^{5/2}}$	$= -11.0533 \pm 0.0026$ $\text{cal}_{15} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$, or entropy units
Sackur-Tetrode constant, alternative form	S_0/R_0'	$= -5.5643_9 \pm 0.0009$
	$S_0' (= S_0 + R_0' \ln R_0''')$	$= -2.2985_2 \pm 0.0018$ $\text{cal}_{15} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$
Chemical constant (unit at. wt., pressure in dynes $\cdot$ cm^{-2})		
	$= \frac{3}{2} \log \frac{2\pi k^{5/2}}{N_0 h^2}$	$= +4.4174_6 \pm 0.0004$
Same (pressure in atmospheres)	$i_0' = i_0 - \log A_n$	$= -1.5882_5 \pm 0.0004$
Debye-Hückel constant for electrolytes	$(\pi e^6/k^3)^{1/2}$	$= (2.512_{51} \pm 0.004) \times 10^5$ *es*-unit^3 $\cdot$ $\text{erg}^{-3/2} \cdot \text{deg}^{3/2}$
Multiplier of (Curie constant)$^{1/2}$ to give magnetic moment per molecule	$(3k/N_0)^{1/2}$	$= (2.604_{17} \pm 0.003) \times 10^{-20}$ $\text{erg}^{1/2} \cdot \text{deg}^{-1/2} \cdot \text{mole}^{1/2}$
Same, to give Bohr magnetons per molecule	$\frac{(3k/N_0)^{1/2}}{\mu_1}$	$= 2.8384_2 \pm 0.0019$ $\text{erg}^{-1/2} \cdot \text{gauss} \cdot \text{deg}^{-1/2} \cdot \text{mole}^{1/2}$

[2] S_0 is to be used in the formula for the entropy of a perfect monatomic gas $S = (3/2) R_0' \ln M + (5/2) R_0' \ln T + R_0' \ln V + S_0$ where M = molecular weight in grams, T = °C abs., V = vol. in cm^3. S_0' is to be used in $S = (3/2) R_0' \ln M + (5/2) R_0' \ln T - R_0' \ln P + S_0'$ where P = pressure in normal atmospheres (A_n).

APPENDIX III

For convenience in simple calculations, the following table of molecular velocities, free paths, and diameters is included. The values are not necessarily accurate and in view of Appendix I, which is much more recent, must be used with caution:

MOLECULAR VELOCITIES, MEAN FREE PATHS, AND DIAMETERS*

Gas	Velocity at 0°C.	Mean free path, L	Molecular diameter	
			η	b
	cm./sec.	cm.	cm.	cm.
Hydrogen, H_2...	18.39×10^4	18.3×10^{-6}	2.47×10^{-8}	2.32×10^{-8}
Helium, He.....	13.11×10^4	28.5×10^{-6}	2.18×10^{-8}	2.30×10^{-8}
Nitrogen, N_2....	4.93×10^4	9.44×10^{-6}	3.50×10^{-8}	3.53×10^{-8}
Oxygen, O_2.....	4.61×10^4	9.95×10^{-6}	3.39×10^{-8}	
Neon, Ne.....	5.61×10^4	19.3×10^{-6}		
Argon, A.....	4.13×10^4	10.0×10^{-6}	3.36×10^{-8}	2.86×10^{-8}
Krypton, Kr....	2.86×10^4	9.49×10^{-6}	.....	3.14×10^{-8}
Xenon, Xe.....	2.28×10^4	5.61×10^{-6}	.....	3.42×10^{-8}
Chlorine, Cl.....	3.07×10^4	4.57×10^{-6}	4.96×10^{-8}	
Methane, CH_4..	6.48×10^4	7.79×10^{-6}		
Ethylene, C_2H_4..	4.88×10^4	5.47×10^{-6}	4.55×10^{-8}	4.68×10^{-8}
Carbon monoxide, CO.....	4.93×10^4	9.27×10^{-6}	3.50×10^{-8}	
Carbon dioxide, CO_2.....	3.92×10^4	6.29×10^{-6}	4.18×10^{-8}	3.40×10^{-8}
Ammonia, NH_3..	6.28×10^4	6.95×10^{-6}		
Nitrous oxide, N_2O.....	3.92×10^4	6.10×10^{-6}	4.27×10^{-8}	
Nitric oxide, NO.	4.76×10^4	9.06×10^{-6}	3.40×10^{-8}	
Sulph. hydrogen, H_2S.....	4.44×10^4	5.90×10^{-6}		
Sulph. dioxide, SO_2.....	3.22×10^4	4.57×10^{-6}		
Hydrochloric acid, HCl.....	4.30×10^4	6.86×10^{-6}		
Water, H_2O.....	7.08×10^4	7.22×10^{-6}	4.09×10^{-8}	

* These values are approximate and are as given by G. W. C. Kaye and T. H. Laby. "Physical and Chemical Constants," Longmans, Green & Co., London, 1911.

APPENDIX IV

For the purpose of facilitating computations involving mean free paths and problems such as ionization by collision, the following table of exponential functions is included:

EXPONENTIAL FUNCTIONS

x	e^x	e^{-x}	x	e^x	e^{-x}
0.0	1.0000	1.000000	5.0	148.41	0.006738
0.1	1.1052	0.904837	5.1	164.02	0.006097
0.2	1.2214	0.818731	5.2	181.27	0.005517
0.3	1.3499	0.740818	5.3	200.34	0.004992
0.4	1.4918	0.670320	5.4	221.41	0.004517
0.5	1.6487	0.606531	5.5	244.69	0.004087
0.6	1.8221	0.548812	5.6	270.43	0.003698
0.7	2.0138	0.496585	5.7	298.87	0.003346
0.8	2.2255	0.449329	5.8	330.30	0.003028
0.9	2.4596	0.406570	5.9	365.04	0.002739
1.0	2.7183	0.367879	6.0	403.43	0.002479
1.1	3.0042	0.332871	6.1	445.86	0.002243
1.2	3.3201	0.301194	6.2	492.75	0.002029
1.3	3.6693	0.272532	6.3	544.57	0.001836
1.4	4.0552	0.246597	6.4	601.85	0.001662
1.5	4.4817	0.223130	6.5	665.14	0.001503
1.6	4.9530	0.201897	6.6	735.10	0.001360
1.7	5.4739	0.182684	6.7	812.41	0.001231
1.8	6.0496	0.165299	6.8	897.85	0.001114
1.9	6.6859	0.149569	6.9	992.27	0.001008
2.0	7.3891	0.135335	7.0	1096.6	0.000912
2.1	8.1662	0.122456	7.1	1212.0	0.000825
2.2	9.0250	0.110803	7.2	1339.4	0.000747
2.3	9.9742	0.100259	7.3	1480.3	0.000676
2.4	11.023	0.090718	7.4	1636.0	0.000611
2.5	12.182	0.082085	7.5	1808.0	0.000553
2.6	13.464	0.074274	7.6	1998.2	0.000500
2.7	14.880	0.067206	7.7	2208.3	0.000453
2.8	16.445	0.060810	7.8	2440.6	0.000410
2.9	18.174	0.055023	7.9	2697.3	0.000371
3.0	20.086	0.049787	8.0	2981.0	0.000335
3.1	22.198	0.045049	8.1	3294.5	0.000304
3.2	24.533	0.040762	8.2	3641.0	0.000275
3.3	27.113	0.036883	8.3	4023.9	0.000249
3.4	29.964	0.033373	8.4	4447.1	0.000225
3.5	33.115	0.030197	8.5	4914.8	0.000203
3.6	36.598	0.027324	8.6	5431.7	0.000184
3.7	40.447	0.024724	8.7	6002.9	0.000167
3.8	44.701	0.022371	8.8	6634.2	0.000151
3.9	49.402	0.020242	8.9	7332.0	0.000136
4.0	54.598	0.018316	9.0	8103.1	0.000123
4.1	60.340	0.016573	9.1	8955.3	0.000112
4.2	66.686	0.014996	9.2	9897.1	0.000101
4.3	73.700	0.013569	9.3	10938	0.000091
4.4	81.451	0.012277	9.4	12088	0.000083
4.5	90.017	0.011109	9.5	13360	0.000075
4.6	99.484	0.010052	9.6	14765	0.000068
4.7	109.95	0.009095	9.7	16318	0.000061
4.8	121.51	0.008230	9.8	18034	0.000055
4.9	134.29	0.007447	9.9	19930	0.000050
5.0	148.41	0.006738	10.0	22026	0.000045

APPENDIX V

For the purpose of facilitating computations, a table of values of the energy distribution function e^{-x^2}, its integral, and the function $\psi(x)$ has been included:

TABLE OF VALUES FOR e^{-x^2} AND $\psi(x)$

x	e^{-x^2}	$\frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}dx$	$\psi(x)$
0.1	0.99905	0.11246	0.20066
0.2	0.96080	0.22270	0.40531
0.3	0.91393	0.32863	0.61784
0.4	0.85214	0.42839	0.84200
0.5	0.77880	0.52050	1.08132
0.6	0.69768	0.60386	1.33907
0.7	0.61263	0.67780	1.61819
0.8	0.52729	0.74210	1.92132
0.9	0.44486	0.79691	2.25072
1.0	0.36788	0.84270	2.60835
1.1	0.29820	0.88021	2.99582
1.2	0.23693	0.91031	3.41448
1.3	0.18452	0.93401	3.86538
1.4	0.14086	0.95229	4.34939
1.5	0.10540	0.96611	4.86713
1.6	0.07730	0.97635	5.41911
1.7	0.05558	0.98379	6.00570
1.8	0.03916	0.98909	6.62715
1.9	0.02705	0.99279	7.28366
2.0	0.01832	0.99532	7.97536
2.1	0.01215	0.99702	8.70234
2.2	0.00791	0.99814	9.46467
2.3	0.00504	0.99886	10.26236
2.4	0.00315	0.99931	11.09547
2.5	0.00197	0.99959	11.96402
2.6	0.00116	0.99976	12.86798
2.7	0.00068	0.99987	13.80734
2.8	0.00039	0.99992	14.78225
2.9	0.00022	0.99996	15.79255
3.0	0.00012	0.99998	16.83830

APPENDIX VI

Values of definite integrals of the form $\int u^n e^{-hmu^2} du$, from 0 to ∞ for various values of n:

$$\int_0^\infty e^{-hmu^2} du = \frac{1}{2}\sqrt{\frac{\pi}{hm}}$$

$$\int_0^\infty e^{-hmu^2} u du = \frac{1}{2hm}$$

$$\int_0^\infty e^{-hmu^2} u^2 du = \frac{1}{4}\sqrt{\frac{\pi}{h^3m^3}}$$

$$\int_0^\infty e^{-hmu^2} u^3 du = \frac{1}{2h^2m^2}$$

$$\int_0^\infty e^{-hmu^2} u^4 du = \frac{3}{8}\sqrt{\frac{\pi}{h^5m^5}}$$

$$\int_0^\infty e^{-hmu^2} u^5 du = \frac{1}{h^3m^3}$$

$$\int_0^\infty e^{-hmu^2} u^6 du = \frac{15}{16}\sqrt{\frac{\pi}{h^7m^7}}$$

$$\int_0^\infty e^{-hmu^2} u^7 du = \frac{3}{h^4m^4}$$

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the kinetic theory of gases

by Leonard B. Loeb

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